Development of a Simplified Electrochemical Noise Method to Monitor Assets Under Insulation

By

©Susan Caines

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Dedicated to

my husband and children

for their unwavering

support and encouragement

ABSTRACT

Corrosion under insulation (CUI) is a serious problem in many industries both on and offshore. When operations are conducted in marine environments the opportunity for CUI is increased due to the harsh environment created by salt water. CUI can damage equipment and piping systems leading to loss of product containment which puts personnel and production in jeopardy. This research determines the current understanding of CUI, methods available for determining corrosion rates and develops a simplified electrochemical noise method to determine and predict CUI through laboratory and field operations.

From the high level CUI literature review two areas for further investigation were determined. Pitting corrosion was identified as a significant area of study and as it is as a key mechanism of pipe failure in offshore operations. Electrochemical noise was found to be a promising technique for monitoring CUI due to its ability to identify corrosion mechanism as well as corrosion rate.

Two objectives for research were identified:

1. To generate corrosion under insulation data
2. To develop a continuous monitoring technique for assets under insulation

To satisfy the objective of CUI data generation a comprehensive experimental plan was developed. This plan develops a field test procedure to study corrosion under insulation (CUI) in marine environments that ensures that data collected is

representative of CUI developed in the offshore industry. The experimental design was completed and the facilities and equipment installed with monitoring and analysis of the ongoing experiment will be completed over the next three years.

This research developed, verified and applied a simplified EPN method to monitor corrosion. This method can be used to recognise different corrosion mechanisms (localized/uniform) and to estimate corrosion rates. A relationship between isolated electrode EPN, mass loss and corrosion rate was established. The simplified method aided in determining that there is increased corrosion activity under insulation due to retained moisture at the pipe surface.

The completion of this research expanded the understanding of how and when CUI occurs, developed new and developed a new simplified electrochemical noise method for online monitoring of CUI. These successes will ultimately improve offshore operations; both improving safety and production.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INDEX OF TERMS

A	Current
AE	Acoustic emission
ASM	American Society for Metals
ASTM	American Society for Testing and Materials
AUV	Autonomous Underwater Vehicles
CF	Consequence of failure
CLSM	Confocal Laser Scanning Microscopy
CR	Corrosion Rate
CUI	Corrosion Under Insulation
DMM	Digital multi-meter
DNV	Det Norske Veritas
DOE	Design of Experiments
ECN	Electrochemical Current Noise
ER	Electrical resistance

EN	Electrochemical noise
EPN	Electrochemical Potential Noise
EW	Equivalent weight
FFS	Fitness-for-service
JIS	Japanese Industrial Standard
LPR	Linear Polarization resistance
LTCS	Low temperature carbon steel
MAWP	Maximum allowable working pressure
MR	Mass loss rate
NDT	Non-destructive techniques
PPR	Pit propagation rate
PF	Probability of failure
QRA	Quantitative risk analysis
RAM	Risk assessment methods
RBI	Risk-based Assessment
RE	Reference Electrode
RFID	Radio-frequency identification
ROV	Remote operated vehicles
RP	Recommended practice
SCC	Stress corrosion cracking
SCE	Saturated calomel electrode
TOW	Time of wetness
V	Potential

WBE	Wire beam electrode
WE	Working Electrode
ZRA	Zero resistance ammeter

1.0 Introduction and Overview

Corrosion under insulation (CUI) is a serious problem in many industries both inland and offshore (Frudge & Bishop , 2008; Simpson, 2007; Fitzgerald et al, 2003). CUI occurs in the space between the metallic component surfaces the insulation when moisture penetrates the system to reach the surface. When operations are conducted in marine environments the opportunity for CUI is increased due to the harsh environment created by high moisture and chlorides in salt water. CUI can damage equipment leading to loss of product containment which puts personnel and production in jeopardy.

Insulation is important to offshore operations and is used to regulate operational temperatures and to protect personnel from injury from extreme temperature components (Delahunt, 2003). Insulation can vary in size and composition and each couple (component and insulation) are designed for the specific application. Insulated components such as pipes are designed to reduce heat losses and to protect asset surfaces from moisture however this is not always possible in all operations. The application of insulation can cause operational issues when corrosion occurs under the insulation. There are many reasons for incomplete protection of pipes; Insulation can be installed incorrectly, difficult geometry can make complete protection impossible, and use and wear of insulation can cause inconsistent protection. All these issues and more can allow for moisture to reach surfaces creating opportunity for CUI. Figure 1 shows the annular space that

insulation can create around the pipe surface that can entrap moisture and create corrosion conditions.

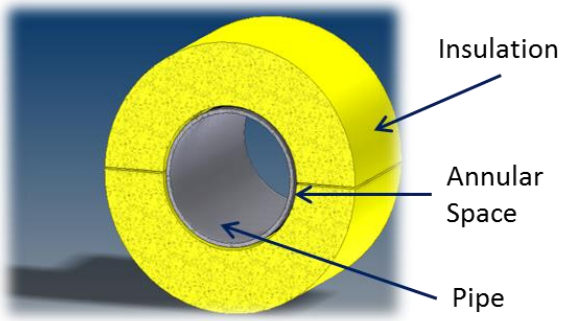

Figure 1: Pipe under insulation demonstrating annular space

If moisture is able to reach the surface in marine environments, chlorides can lead to severe corrosion of steel components. CUI can take many forms in marine environments including localized corrosion, uniform corrosion, and stress corrosion cracking. Uniform corrosion and localized corrosion are the likely corrosion mechanisms of steel piping under insulation and pitting corrosion is thought to be the most common type of localized corrosion (Roberge P. R., 2008) and along with uniform corrosion is included in this research.

CUI is more difficult to detect than other forms of corrosion because insulation prevents direct observation of the surface. This makes identifying and controlling CUI difficult. Most operations employ non-destructive evaluation techniques in their maintenance plans to seek out areas of CUI. As there are significant portions of operations under insulation, evaluation of all systems is not always possible due to time and economic considerations. Due to these constrains, it is possible for corrosion to continue without being identified until loss of containment is reached.

Understanding CUI is important to improving offshore operations. To do this a thorough review of current practises in combating CUI was completed that lead to a focus on pitting corrosion. This analysis led to a comprehensive experimental plan to systematically evaluate CUI in both laboratory and field experiments. This experimental design highlighted gaps in monitoring techniques for CUI. A simplified method for monitoring CUI using electrochemical potential noise was developed and verified through laboratory testing. This method was incorporated into field testing and will lead to a real time monitoring method for CUI.

1.1 CUI Literature review

A literature review of CUI was conducted to understand the current state of knowledge of the phenomenon. A general review of CUI was followed by an in-depth review of pitting corrosion. A review of Electrochemical noise techniques as potential technique for corrosion monitoring was also undertaken

1.1.1 Corrosion under insulation

Current understanding of CUI is generally limited to standards, recommended practises and guidelines that deal with how to combat and predict CUI.

These standards include:

- API 579-1/ASME FFS-1(2007). Fitness-for-service.
- API RP 580 (2009), API recommended practice 580: Risk-based inspection.

- API RP 581 (2008), API recommended practice 581: Risk-based inspection technology.
- ASTM Standard G189, A. (2007), Laboratory Simulation of Corrosion Under Insulation.
- DNV-RP-G101(2002), Recommended practice, Risk based inspection of offshore topsides static mechanical equipment.
- NACE SP0198 (2010), Control of Corrosion Under Thermal Insulation and Fireproofing Materials.
- Winnik, S (Ed.)(2008). Corrosion-Under-Insulation (CUI) Guidelines

Standard inspection techniques and recommended practices that can be applied to CUI are detailed in industry standards. These standards detail how to use non-destructive methods to inspect for corrosion and NACE standard practice “Control of Corrosion Under Thermal Insulation and Fireproofing Materials” describes inspection and maintenance planning to combat CUI (NACE SP0198, 2010). Risk based inspections (RBI) are also commonly used in industry to develop inspection plans to detect CUI (DNV RP-G101, 2002) (API RP 580, 2009), (API RP 581, 2008). Another resource for combating CUI is the European Federation of Corrosion Publications number 55 edited by S. Winnik, “Corrosion-Under-Insulation (CUI) Guidelines” (Winnik 2008).

An experimental design to study CUI in harsh marine environments is the most practical way forward to recognise and study the unknowns. The study includes a

thorough literature review of current CUI understanding and found no published works that evaluate CUI in harsh marine conditions outside of a laboratory. It was found that rates used to evaluate CUI in marine environments are based on short term laboratory testing (Klassen & Roberge, 2003, Engelhardt, Urquidi-Macdonald, & Macdonald, 1997, Engelhardt & Macdonald, 2004). It was also found that the conventional power model ($C(t)=A\,t^{B}$) for corrosion loss (Roberge P. R., 2008) does not account for corrosion mechanism changes over time and should not be used for long term corrosion evaluation. Melcher (2003, 2004, 2008) demonstrated a phenomenological model that allows for changes in corrosion rate due to changes in mechanism. His model is applicable to pitting corrosion in marine immersion and may be applicable to CUI investigation.

Review of current CUI understanding is also included. This review found that beyond standards there is limited work completed to specifically study CUI or methods to predict future corrosion behaviour of assets under insulation. This review included current asset integrity, fitness for service and risk based inspection methods that included corrosion with little or no mention of CUI.

1.1.1.1 CUI Literature Review Outcome

The review of CUI found that there is no commonly used method to assess CUI and limited experimental data available for analysis. There is no widely accepted method for determining long-term corrosion rates. Methods to assess corrosion without insulation were reviewed for their applicability to CUI study.

Review of asset integrity and fitness for service found that while there are methods available there is limited information available for the corrosion rates used in these methods. These methods intend for independent corrosion rate development by users.

There are well established procedures for risk based inspection however there is limited information on probability modeling for corrosion and less specifically for corrosion under insulation.

From the high level CUI literature review pitting corrosion was identified as a significant area of study and as it is as a key mechanism of asset failure in offshore operations.

1.1.2 Pitting Corrosion

Pitting corrosion was found to be the most common and most insidious form of corrosion likely under insulation. When reviewing the current understanding of pitting corrosion in Marine Environments six (6) categories were reviewed. These categories were:

1. Identification of pitting
2. Experimental Methods
3. Mechanism of pitting
4. Modeling of pitting corrosion rates

5. Remaining life assessment model
6. Risked Based Inspection

Each category was reviewed and analysed for depth and breadth of knowledge available. The review found that the largest knowledge gap in understanding Pitting corrosion is the mechanism of pitting corrosion (category 3) and the prediction of pitting corrosion rates (category 4).

1.1.2.1 Pitting Corrosion Literature Review Outcome

There are models available that may predict the failure rate of insulated assets once a precise model of CUI corrosion rate is known (DNV RP-G101, 2002; API 579, 2007; BS 7910; FITNET, 2006; Hodges, et al., 2010; Thodi, Khan, & Haddara, 2009; Race, Dawson, Stanley, & Kariyawasam, 2007; Akmar Mokh & Ismail, 2011).

There are models of corrosion rate available for many environments (Svintradze & Pidaparti, 2010; Engelhardt, Urquidi-MacDonald, & MacDonald, A Simplified Method for Estimating Corrosion, 1997; Valor, Caleyo, Alfonso, Rivas, & Hallen, 2007; Provan & Rodrı´guez III, 1989; Melchers & Jeffrey, 2008; Melchers, 2003) such as buried pipelines (Caleyo, Velázquez, Valor, & Hallen, 2009). These models indicate the importance of different variables that play a critical role in CUI modeling and thus can be used in failure model development.

The review found that there is no standardised method to determine pitting rates, that there is limited agreement between long term pitting behaviour and current

accelerated laboratory testing, and that corrosion rate modeling is needed to improve fitness for service and risk based inspection applications.

Electrochemical noise was found to be a promising technique for monitoring CUI due to its ability to identify corrosion mechanism including pitting as well as corrosion rate.

1.1.3 Electrochemical noise

Electrochemical noise (EN) is a passive method of corrosion monitoring where no applied current or potential is required (Frankel, 2008). This method records deviation from the naturally occurring electrochemical potential and current (Reiner & Bavarian, 2007; Huet, 2006) indicating when corrosion occurs. Pitting and other forms of localised corrosion have been detected using this method with good correlation (Estupiñán-Lópezst al. 2011). EN is a technique used primarily in laboratory work to evaluate corrosion rates and identify corrosion mechanism. EN was first discussed by Iverson (1968) and has been explored and developed since that time. When corrosion occurs, measurable changes in free corrosion current and potential can be measured. This technique evaluates naturally occurring corrosion without external inputs that could affect the results.

EN is evaluated by analysing either (or both) voltage and current noise on a corroding system. EN methods have been widely researched and developed for

corrosion evaluation and study. A comprehensive review of EN methods is presented in chapter4 of this thesis.

EN can be a useful tool in determining corrosion rates and in determining corrosion mechanism such as pitting. Naing, Wong, & Tan (2006) developed a new technique to evaluate CUI that applies EN to determine moisture penetration under insulation using Wire Beam Electrode (WBE) methods. These methods measure potential change against a Saturated Calomel Electrode (SCE) reference electrode. They determined that a WBE sensor could be used to monitor moisture penetration through different types of simulated insulation using noise signature analysis.

1.1.3.1 Electrochemical Noise Literature Review Outcome

Electrochemical noise techniques can be used to determine both corrosion rate and corrosion mechanism. However, they are difficult to apply outside of a controlled laboratory. Current methods use sophisticated and sometimes expensive equipment that require specially trained personnel for interpretation. Measurement of current (A) was found to be especially difficult in field applications.

1.2 Motivation

The motivation of the research work presented in this thesis was to identify the knowledge gaps and develop a potential way forward in understanding the effects of insulation on assets in offshore operations. These knowledge gaps were

identified through a thorough review and analysis of corrosion under insulation, pitting corrosion, and electrochemical noise techniques. The knowledge gaps were identified as follows:

1. There is limited long-term data available to study CUI. This information is needed to develop methods for predicting the long term behaviour of assets under insulation.
2. Current accelerated testing does not accurately reflect in-situ, long term corrosion data.
3. There is no reliable, simple, affordable, on-line continuous direct monitoring of assets under insulation.

These knowledge gaps were used to define the scope of the research work.

1.3 Scope and Objectives

The scope of this research to address identified knowledge gaps that includes the design of experiments for field and laboratory tests, the experimental design for field and laboratory work and the development and verification of a simplified electrochemical potential noise method.

This thesis considers the following research questions:

i. Can reliable long-term CUI data be captured in a field setting?
ii. Can an accelerated test be developed with strong correlation to long term field data?

iii. Can an electrochemical noise monitoring technique be adapted to record field data?

iv. Can traditional electrochemical noise techniques be modified to create a monitoring technique that can estimate corrosion rate and corrosion mechanism?

v. Can electrochemical noise be used to determine if corrosion is intensified when an asset is under insulation?

Considering these research questions, this work identified two significant objectives:

1. To generate corrosion under insulation data: A comprehensive experimental plan was developed. Chapter 3 develops a plan to generate long-term CUI data from field experiments, characterize CUI through laboratory work and lays out a method to develop an accelerated test to generate long term CUI data using a laboratory set-up.
2. To develop a continuous monitoring technique for assets under insulation: A simplified electrochemical potential noise method was developed in Chapter 4 and applied to piping under insulation in Chapter 5.

The monitoring and analysis of the field test data is beyond the scope of this work. This will be carried out by others within the research group. Also beyond the scope of this work is the set-up and completion of the accelerated testing

method experimental plan. This work requires completion of the field test and will be completed by the research group.

1.4 Contribution and Novelty

Corrosion of assets under insulation is a significant issue and no consensus is available on how to best recognise, combat, prevent or predict it is available. This research identifies this need and seeks to lessen the knowledge gap to further understand CUI. To do this, an experimental plan for field testing was developed, this plan built on existing atmospheric testing and laboratory standards to design a plan that would result in long term CUI data that includes both physical corrosion results (mass loss, visual inspection) and electrochemical data to determine corrosion rate and mechanism.

Electrochemical noise techniques are available that can predict corrosion rate and help determine corrosion mechanism. There are many issues with current techniques that make them incompatible in-situ monitoring of assets under insulation including the cost of specialised equipment, difficult data analysis, and electrode similarity constraints. The development of the simplified electrochemical noise technique makes long-term continuous monitoring of assets possible and includes steps to disconnect the traditional coupled potential information to allow for analysis of individual components under investigation. The ability to study individual components (electrodes) using the simplified method can potentially

remove the electrode similarity constraint and further increase the applicability of this method to different assets in industrial operations.

1.5 Organization of thesis

This thesis is written in manuscript format and includes 4 individual papers. The format for this thesis is illustrated in Figure 2.

Chapter 1 includes an overview of the thesis work and a summary of the literature review. The high level literature review of CUI identified pitting corrosion, as a key area for further study.

Chapter 2 reviews and analyses the current understanding of pitting corrosion under insulation. Six (6) categories were reviewed to fully understand the current knowledge of pitting. The study identifies pitting mechanism and pitting corrosion rate prediction as two categories that require further study and identifies the lack of long term corrosion data for CUI as an ongoing issue to develop new methods to predict long-term behaviour. This chapter was published in the Journal of Loss Prevention in the Process Industries 2013: Vol 26, Issue 6, pg 1466-1483.

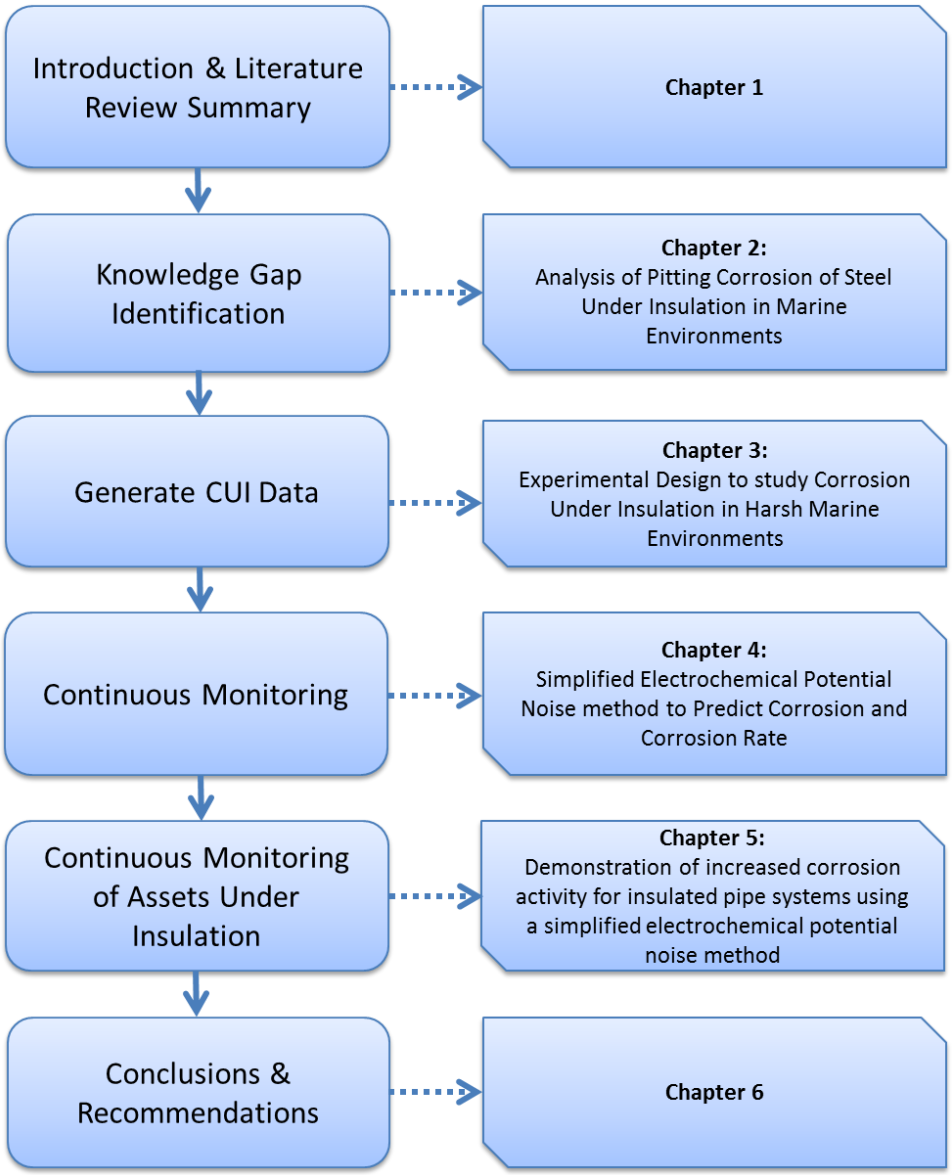

Figure 2: Structure of the thesis

Chapter 3 describes the development of long term testing to study CUI in both laboratory and field experiments to begin to fill the knowledge gap identified in Chapter 2. Three stages of experimentation are developed and include a three year field test, laboratory testing to characterise CUI and the development of an accelerated testing plan to generate long term corrosion rates. The need for a

continuous monitoring technique was also identified in this work. This chapter was published in the Journal of Loss Prevention in the Process Industries 2015: Vol 33, pg 39-51.

Chapter 4 describes the development of a simplified electrochemical potential noise (EPN) technique that uses a three identical electrode set-up and isolates individual electrode EPN to predict corrosion rate (Caines et al. 2016). This technique is needed to characterise corrosion behaviour in long term field testing (Caines et al. 2016). This chapter was submitted for publication to the Journal of Loss Prevention in the Process Industries. Peer feedback received, paper is revised and resubmitted, awaiting final decision (as of October 2016).

Chapter 5 applies the simplified EPN method developed in Chapter 4 to demonstrate the increased corrosion activity observed in pipes under insulation. This work highlights the differences in corrosion behaviour under insulation and further validates the applicability of the simplified EPN method for use in field and industrial applications. This chapter is currently in peer review process in the Journal of Loss Prevention in the Process Industries.

Chapter 6 summarises the findings of the thesis and reports the main conclusions form all work. Recommendations for future work are also included in this chapter.

1.6 Co-authorship Statement

The PhD Candidate, Susan Caines is the first author of the publication, and is the main contributor to this work. Co-authors contributed at all stages of the research: aid in developing the concept, facilitating the experimental setup, analyzing the data and its interpretation. First author, Susan Caines, prepared the first draft of all the manuscripts while coauthors have reviewed and revised the draft. With all authors consent work was submitted and published (Caines et al. 2013, Caines et al. 2014, Caines et al. 2016, Caines et al. 2016b).

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2.0 Analysis of Pitting Corrosion of Steel Under Insulation in Marine Environments

Preface

A version of this paper was published in in the Journal of Loss Prevention in the Process Industries. The primary author is Susan Caines and the co-authors for this manuscript include Dr. Faisal Khan and Dr. John Shirokoff. The primary author developed the conceptual model, completed the literature review and analysis and prepared the first draft of the manuscript. The co-author Faisal Khan helped in developing the concept, reviewing and correcting the analysis and contributed in, reviewing and revising the manuscript. Dr. Shirokoff contributed through support in the development and assisted in reviewing and revising the manuscript. Minor editing of the published paper was completed to conform to formatting and to correct errors.

Abstract

Corrosion under insulation (CUI) is an important issue in marine environments. Pitting corrosion is a significant contributor to this issue. The ability to understand and model pitting behavior is integral to designing and maintaining assets in marine environments to decrease costs and increase safety and productivity. This paper reviews and analyses six categories of pitting knowledge to assess the

current depth and breadth of understanding and to identify knowledge gaps in each category. The categories investigated are: identification of pitting, experimental methods, mechanism of pitting, modeling of pitting corrosion rates, remaining life assessment modeling, and risked based inspections. This analysis finds that the depth of knowledge on pitting corrosion rate modeling and pitting mechanism is limited and requires further detailed study. The outcome of such study will strengthen pitting corrosion rate modeling, the accuracy of fitness for service assessments and risk-based inspection strategies.

Keywords

Pitting corrosion, corrosion under insulation, safety assessment, fitness-for-service assessment, risk-based inspection

Abbreviations

AE	Acoustic emission
ASM	American Society for Metals
ASTM	American Society for Testing and Materials
AUV	Autonomous Underwater Vehicles
CF	Consequence of failure
CLSM	Confocal Laser Scanning Microscopy
CUI	Corrosion Under Insulation
DNV	Det Norske Veritas
EN	Electrochemical noise
FFS	Fitness-for-service

JIS	Japanese Industrial Standard
MAWP	Maximum allowable working pressure
NDT	Non-destructive techniques
PPR	Pit propagation rate
PF	Probability of failure
QRA	Quantitative risk analysis
RAM	Risk assessment methods
RBI	Risk-based Assessment
ROV	Remote operated vehicles
RP	Recommended practice
SCC	Stress corrosion cracking
TOW	Time of wetness

2.1 Introduction

Corrosion under insulation (CUI) is a serious issue in marine environments. This type of damage can have catastrophic effects on production losses, health and safety, and the environment in the offshore industry if it is not identified before it degrades to a level where containment is threatened. CUI can take many forms in marine environments including pitting, uniform corrosion, and stress corrosion cracking. CUI can occur when moisture penetrates the insulation and helps to create a corrosion cell. This can occur in many ways including insulation damage or wicking, atmospheric wetness, or poor installation. If the component has a protective coating, breaks or holidays in the protective layer are also needed to

expose the underlying metal to moisture. Pitting corrosion is thought to be the most common type of localized corrosion (Roberge P. R., 2008) and is the focus of this review.

Pitting is a form of corrosion observed in some metals where corrosion is localized to small areas of degradation. It can lead to catastrophic consequences in marine applications. Small pits can progress through wall thickness and lead to a lack of containment of process materials or act as initiation site for stress corrosion cracks that can also lead to lack of containment. Brittle fracture of components is an issue. If pitting develops such that the strength of the member is affected, brittle failure can occur. This type of failure can be catastrophic and lead to a complete lack of containment or structural integrity of components.

The ability to predict pitting behaviour is key to designing and maintaining assets in marine environments. If realistic models are not available, conservative corrosion rates are used and can lead to increased costs and decreased productivity.

Numerous studies and scholarly works have been done on the pitting behaviour in steel for marine applications. The work varies from understanding how to identify pitting to predicting the likelihood of pitting and how it affects the service life of components. Studies on failure under insulation due to pitting in petrochemical applications have been conducted (Suresh Kumar, Sujata, Venkataswamy, &

Bhaumik, 2008); however, no specific information on pitting under insulation in marine environments was found. Available literature was reviewed to determine the current state of understanding of pitting corrosion.

When reviewing the current understanding of pitting corrosion, the study was divided into 6 categories and the depth and breadth of available work analysed to identify knowledge gaps in each category. The categories are:

1. Identification of pitting
    - Inspection techniques
    - Non- destructive evaluation
2. Experimental Methods
    - Simulating pitting behaviour
3. Mechanism of pitting
    - Phases of pitting
    - Causes of pitting
    - Factors effecting pitting potential
4. Modeling of pitting corrosion rates
    - Models to predict corrosion rate
5. Remaining life assessment model

6. Risked Based Inspection

    - Predicting inspection/maintenance based on severity and susceptibility to pitting corrosion

2.1.1 Rating System for Depth and Breadth of Pitting Knowledge

A qualitative rating system was developed to characterise the literature in terms of understanding and application of monitoring, predicting, preventing, and controlling pitting in marine environments. Table 1 below illustrates the rating system.

Table 1: Rating system for Depth and Breadth of Knowledge

Score	Nil = 0	Low = 1-3	Mid = 4-6	High = 7-9	Complete=10
Depth	No understanding of topic	High Level (shallow) understanding of topic. General concept is understood	Topic is understood. Competing theories by subject matter experts.	Consensus between subject matter experts on topic.	Complete understanding of topic.
Breadth	No demonstration of broad application of theory	Limited application across fields	Increasing application of knowledge across environments/industries	Demonstrated application across environments/industries	Complete demonstration of broad application of theory

The six designated categories of pitting in marine environments are summarised in the following sections. Each section includes an overview of current understanding and the depth and breadth of knowledge is identified.

2.2 Categorized Review and Analysis

The six categories of pitting are reviewed, analysed, and summarised in the following sections.

2.2.1 Identification of pitting

The first step in understanding pitting in steel is to correctly identify the phenomenon. Pitting corrosion is characterised by small blemishes in the surface of a material. Figure 3 illustrates pits on stainless steel in a simulated marine environment.

Figure 3: Pits on 304 stainless steel after exposure to simulated marine environment (3.5g of NaCl per litre H2O) (Caines, 2013)

Pits can form in many different shapes and sizes. Figure 4 shows some typical cross sections of pits. The danger in pitting is that the size of the pit opening at the surface is not always indicative of the amount of sub-surface corrosion. This can lead to structural instabilities in components that may appear to have little surface damage.

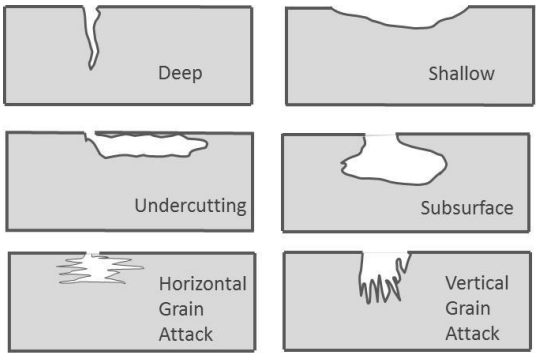

Figure 4: Typical cross-sectional shapes of corrosion pits (Roberge P. R., 2008) (Phull, 2003).

While shallow pits are easier to examine and are unlikely to affect the structural integrity of the component, they can act as stress concentrators and initiate stress corrosion cracking (SCC). SCC is another corrosion mechanism seen under insulation in marine environments. Its contribution to CUI is also explored in this work.

There are many techniques that can identify the presence of pitting. This part of pitting corrosion is well understood and well documented by (Davies & Scott, 2003), (McIntyre & Vogelsang, 2009), (Roberge P. R., Corrosion Inspection and Monitoring, 2007), and (Phull, 2003). The main techniques identified in the American Society for Metals (ASM) Handbook (Phull, 2003) to identify pitting are as follows:

1. Visual inspection
2. Metallographic examination
3. Mass loss

4. Pit depth measurement

5. Non-destructive Inspection

2.2.1.1 Visual inspection

The American Society for Testing and Materials (ASTM) Standard G46 “Standard Guide for Examination and Evaluation of Pitting Corrosion“ (ASTM G46, 2005) describes visual inspections as inspection that can be done in ambient light to determine location and severity of pitting. Pictures are often used to document the difference in appearance of pits before and after removal of corrosion products. This technique is the easiest to employ, requires no specialised equipment and is relatively inexpensive. More detailed descriptions of visual inspections are well documented in (Roberge P. R., Corrosion Inspection and Monitoring, 2007), (Byars, 1999), (Visual Inspection, Nondestructive Evaluation and Quality Control, 1989), and (Heidersbach, 2011).

More complex visual inspection techniques are used to evaluate areas that are difficult or dangerous for personnel to access. These visual inspections are facilitated through use of video and robotics; both remotely operated and autonomous.

Remote operated vehicles (ROVs) attempt to replace human visual inspections to increase safety, reduce cost, and increase efficiency (Terribile, Schiavon, Rossi, & Zampato, 2007). These vehicles use video to allow inspectors to guide and inspect

areas that are difficult to reach and/or are dangerous. ROVs can detect external corrosion, damage, and anode wear in deep water pipelines (Kros, 2011).

Work is being conducted to adapt Autonomous Underwater Vehicles (AUVs) to perform visual inspections in underwater structures and pipelines (Courbot, Nasr, Gilmour, & Biedermann, 2013) (Yu & Ura, 2002) (Mcleod, Jacobson, & Tangirala, 2012). These inspections would include high resolution photographs of the length of the pipe, real-time image processing, and location tagging for future inspection.

2.2.1.2 Metallographic Examination

Metallographic Examination is an investigative technique that can be used to determine the size, shape, and density of corrosion pits. It is one of the most important examination techniques as it can yield quantitate information on pitting corrosion. This technique is also used to verify true pits versus metal dropout from other corrosion mechanisms or to investigate corrosion rate correlation to inclusions and microstructure (ASTM G46, 2005). Figure 5 shows a cross section of a corrosion pit on 316L Stainless steel. Measurements for maximum pit depth (C) and pit width (B) may be recorded as indicated.

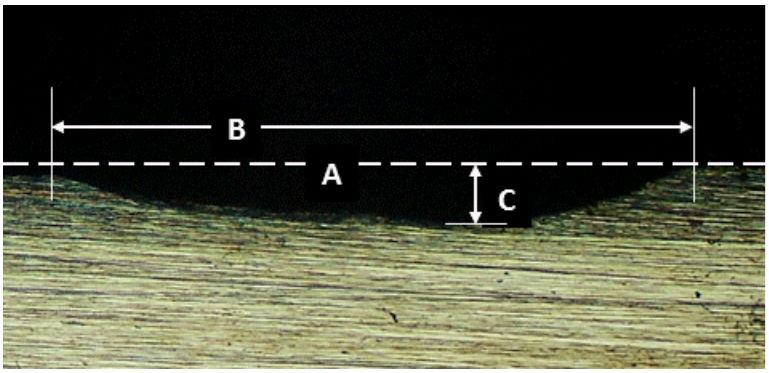

Figure 5: Cross-section of pitting corrosion on 316L stainless steel. A: Original surface, B: Pit with, C: Pit depth (Snow & Shirokoff, 2008)

Metallographic Examination is typically a destructive analysis technique as the specimen must be cut from the component and examined with a microscope. In-situ metallography can be used when removal of the component is not feasible. This type of metallography uses surface replication and does not produce the same quality micrographs as traditional destructive techniques (Jana, 1995).

Simultaneous in-situ optical and electrochemical methods for identifying and measuring pitting corrosion have also been reviewed and measured (Power & Shirokoff, 2012) (Power & Shirokoff 2013). This approach was used to measure corrosion in 316L stainless steel subject to simulated seawater conditions and in industrial sulfuric acid environment simulating hydrometallurgical recovery of metals from nickel sulfide ores. Power and Shirokoff found that this innovative approach to studying the surface microstructural changes in real time could successfully correlate to the electrochemical response at the surface under aerated and deaerated conditions. The technique is a low cost and practical

method to investigate samples under constant temperature conditions in a custom built corrosion cell attached to an electrochemical probe, potentiostat-galvanostat, optical microscope, digital camera, and VHS-VCR-DVD recording system.

Proper surface preparation of samples is important; poor preparation can lead to inaccurate measurements, observation and even destruction of the sample. Sample preparation includes cutting a sample (sectioning), mounting of small samples if needed, cleaning of a surface, and polishing (ASTM E3, 2011), (ASTM G1, 2011). All of these steps must be conducted carefully and appropriately for the material and environmental conditions. Proper care must be taken to ensure the preparation methods do not affect the important surface.

Examples and details of metallography are widely discussed, a few important sources are (Vander Voort, 1999), (Vander Voort, 2004), (ASTM E3, 2011), (ASTM G1, 2011), (Gale & Totemeier, 2004), and (Reardon, 2011).

2.2.1.3 Mass loss

Mass loss techniques are used to determine the amount of material lost due to corrosion. This is accomplished by a systematic measurement of the mass loss over a specific period of time.

The application of mass loss studies to pit evaluation is limited. Mass loss due to this type of localized corrosion can be too small to allow for identification through this method. Some standards for pitting evaluation include mass loss as a possible technique includes (ASTM G46, 2005) and (Phull, 2003). This technique may be

useful if pitting is the predominant corrosion mechanism and the amount of general corrosion in minimal. Other sources do not include mass loss as a viable technique for pitting identification (Heidersbach, 2011), (Jones, 1996), and (Baboian, 2005).

This method is most useful in evaluation of uniform corrosion, corrosion that affects the total surface area of a component. A standard methodology for preparing samples for mass loss evaluation such as ASTM G1:The Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, are used (ASTM G1, 2011).

2.2.1.4 Pit Depth Measurement

Pit depth measurement is a key technique in pit identification and evaluation (ASTM G46, 2005), (Phull, 2003). ASTM G46 (2005) describes different methods to evaluate pit depth. Metallography can be used to evaluate a vertically sectioned pit (ASTM G46, 2005). The depth of the pit can then be measured with a calibrated eyepiece. The limitation of this method is that the deepest pit may not be selected for evaluation. Machining is another method discussed by the standard. This method involves systematic machining of a pitted surface and subsequent thickness measurement to determine pit depth. This method can be used to find the maximum pit depth and to determine the number of pits with specific depths. These two methods are destructive and cannot be used in service. Alternatively, a depth gage may be used in service to determine pit depth. This method uses a calibrated depth inserted into a pit. This method is limited to pits that are large

enough at the base to allow full penetration of the gage and that have not experienced undercutting or a direction change (ASTM G46, 2005).

Jasiczek et al. (Jasiczek, Kaczorowski, Kosieniak, & Innocenti, 2012) have identified a new non-destructive method to evaluate pit depth using Confocal Laser Scanning Microscopy (CLSM) that has shown potential to further the ability to measure pit depth. CLSM creates a three dimensional image of a material surface (Clarke & Eberhardt, 2002) that can be analysed to determine pit depth. The authors showed that this technique can reliably measure pit depth and had the potential to evaluate additional pit characteristics such as diameter and volume.

2.2.1.5 Non-destructive Testing

Non- destructive testing (NDT) is a key technique used in industry to evaluate the current state of components and equipment in service and to aide in maintenance planning. NDT is used to identify, monitor and qualify many types of issues in industry during operations and during short operational shut-downs. Removal of components from a working facility is not practical so NDT becomes more important for defect evaluation.

ASTM Standard G46 (ASTM G46, 2005) describes NDT applicable to identifying pitting corrosion. NDT is well established; however, these techniques are not as effective at characterizing pitting as destructive methods. NDT also requires specialized training to ensure realistic results. Many references are available that describe different types and applications of NDT for pit identification (Roberge P.

R., 2011), (Roberge P. R., Corrosion Inspection and Monitoring, 2007), (Heidersbach, 2011), (Shreir, Jarman, & Burstein, 1994). A brief description of each NDT is presented below.

2.2.1.6 Radiography

Pitting is readily detected by radiography and this technique is routinely applied in service identify and monitor corrosion (Heidersbach, 2011). In this technique, radiation/X-rays passes through the component under investigation and the intensity of the exit rays indicates changes in thickness. To successfully identify pits, the depth must be larger than 0.5% of the metal thickness (ASTM G46, 2005). This technique can quickly identify corrosion issues however, only small areas are inspected at a time, the 2D image gives no depth information and access to both sides of a component is required (Heidersbach, 2011).

When a component is insulated, the insulation has traditionally been removed for inspection and identification of pitting. This is a time consuming and costly operation. Pachacek (2003) introduced a new method for inspecting insulated vessels using profiler portable real-time radiography (PPRTR) (Pachacek, 2003). This technique can quickly identify areas of concern, both gradual loss, indicating general corrosion and abrupt wall thickness changes indicated localized (pitting) corrosion. This method allows for more thorough coverage of long insulated pipe lengths and can identify areas that require further NDT to determine action.

2.2.1.7 Electromagnetic

This type of evaluation technique includes eddy current, magnetic particle, and microwave techniques (Rao, Jayakumar, & Raj, 2007). These techniques are used on electrically conducting materials and use induced magnetic fields to detect defects (ASTM G46, 2005). The discontinuities in the material are identified by their effect on electrical conductivity or magnetic permeability or dielectric permittivity.

2.2.1.8 Sonics

This technique uses sound energy to find the size and location of pits.

Pellegrino et al. (Pellegrino & Nugent, 2012) investigated remote visual inspection (RVI) with 3D phase measurement to size pits in compressor blades and the characterization of pipe wall pitting with phase-array ultrasonic testing (PAUT) with dual transducer. They report that new 3D phase measurement technology can measure pits with diameters as small as 0.1 mm and depths as shallow as 0.025 mm. They indicate that these measurements are accurate and can be conducted quickly. Traditional ultrasonic transducers have difficulty accurately measuring and identifying pits. These limitations are due to limited inspection area. PAUT was developed to increase the accuracy through the use of multiple receiver elements. This increases the area inspected and the likelihood of identifying and measuring the deepest pits.

Jirarungsatian et al. (2010) in their paper discuss acoustic emission (AE) as a method for detecting both pitting and uniform corrosion (Jirarungsatian & Prateepasen, 2010). This in-service method detects transient waves from energy released from localized material sources to directly measure corrosion failure mechanisms. They indicate that ambient noise has been the main issue preventing field use of this detection method.

2.2.1.9 Penetrants

Penetrant examination is a non-destructive technique that identifies surface defects on a non-porous surface. Because pitting occurs at the surface, this method is widely used to find and classify pits (Borucki, 1989). This method detects surface pits through the application of a liquid penetrating material; the liquid must penetrate defects through capillary action over the dwell time (Raman, 2007). Intensity of the color and the rate of bleed out both indicate the size of the defect (ASTM G46, 2005), (ASTM E1417, 2013).

There are two types of penetrants, florescent and visible. The appropriate type of penetrant is chosen based on many factors including type of flaw detected, surface condition, and sensitivity required (Borucki, 1989). Fluorescent penetrant is more reliable and sensitive than visible penetrants and are used more often. Visual penetrants are usually red and must be viewed under white light while fluorescent penetrants are typically green and glow under ultraviolet light.

2.2.1.10 Electrochemical Identification

Another method to evaluate pitting corrosion is through the use of electrochemical methods. ASTM has several standards that describe these techniques (ASTM F746, 2009), (ASTM G61, ASTM G61 Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys, 2009), and (ASTM G150, 2010). These techniques use applied current or potential to establish the relative performance of materials in an environment. These techniques are usually applied in laboratory testing. Use of these techniques for on-line monitoring is limited due to the high applied potentials that permanently effect components under evaluation (Phull, 2003).

One newer method of electrochemical monitoring of corrosion that has the potential to be used on-line for the detection of pitting corrosion is electrochemical noise (EN) measurement techniques. EN technique is a passive method of corrosion monitoring as no applied current is required (Frankel G. , 2008). This method measures deviation from the naturally occurring electrochemical potential (Reiner & Bavarian, 2007). This variation is due to corrosion and can be measured. This technique has shown good correlation in detecting the formation of localized corrosion (Estupiñán-López, Martínez-Villafañe, Uruchurtu Ch, & Gaona-Tiburcio, 2011). A single electrode monitoring probe has been successfully used in applications where the structure can be used as a current return path (Eden & Kane, 2005). It is expected that this method can be used to indicate when corrosion

is occurring; however the challenge with electrochemical monitoring is to directly determine corrosion rate in non-immersed applications (Klassen & Roberge, 2003).

2.2.1.11 Innovative Techniques

While there are many standards and related scholarly works describing well established pitting identification methods, new and improved techniques are also being investigated.

Papavinasam et al. (2012) investigated five non-intrusive inspection techniques on test pipes with artificially implanted pits over 12 years (Papavinasam, Doiron, Attard, Demoz, & Rahimi, 2012). Their work established the reliability of each of the techniques based on a number of criteria. Table 2 summarizes their findings as follows.

Table 2: Summary of findings by Papavinasam et al. (2012)

Technique	Reliability	User-friendly	Sensing Element	Area/Sensor Ratio.	Remote Monitor-ing	Boundary and Limitations	Conclusions
Ultrasonic-handheld	Can detect location of defect or pit. Reliable to error of ± 0.25mm	Low set-up time, Portable, applicable for Hazardous field conditions	Piezoelectric crystal to mechanical energy. Determines thickness without accessing the internal pipe surface	manual scanning	No Remote Monitoring, onsite data collection by technician	Requires: physical contact & couplant. Shape influences results. Results dependant on experience and skill.	most ideal, current, non-intrusive technique

Ultrasonic-fixed	Cannot detect location of defect or pit (fixed location). Reliable to error of ± 0.25mm. Cannot be calibrated; long-term reliability not ensured	Longer set-up time. Can be used in hazardous field conditions. Not portable	Piezoelectric crystal to mechanical energy. Determines thickness without accessing the internal pipe surface	N/A. Fixed Location	Theoretically suitable for remote monitoring	Requires: physical contact & couplant. Measurements only at locations where sensors installed (2.5 cm). Results independent of experience and skill after installation.	Development of liquid couplant: Not dry over time and long term adherence to substrate
Electrical probe	Reliability dependant on : number of pins, distance between pins, contact resistance, applied current, and accuracy of resistance measurement instrument	Two (2) options. 1. Permanently spot welded to structure: Low contact resistance, restricted use in some applications and jurisdictions. 2. spot-welded onto pipe section and clamped to structure. Portable with higher contact resistance	Based on Ohm`s Law where resistance is inversely proportional to wall thickness. 2 pins to apply current, 2 pins to measure potential.	Dependant on number of pins. Increased distance between pins, measured area increases, sensitivity to wall loss decreases.	Appropriate for remote monitoring.	Difficulties due to defect geometry. Impractical for large surfaces. Relies heavily on operator skill and experience. No testing or evaluation by regulatory or by standards making body	Establishment of a relationship between geometry of pins, wall thickness, and resistance measurement needed
Hydrogen permeation	indicates cannot be reliably used to measure pitting corrosion rates	Can be moved. No welding, machining or use of epoxies. Surface is not modified.	Measures pressure increase or hydrogen gas.	very small area / sensor	Not suitable for remote monitoring	Does not directly measure wall thickness. Not capable of detecting defect location. Provides a corrosion rate for a general area	Suitable applications required
Fibre-optic	No correlation established between measurements to physical measurement of pit depths	Easy attachment. Very fragile. Difficult to remove once attached.	Cable is both sensor and communicator. Macrostrain of cable measured to determine wall thickness.	Area covered is proportional to length of cable	suitable for remote monitoring	Very new and needs to be proven. Fiber very fragile. No operator training available	Fragile fibers limiting advancement

Another technique described by Holme et al. (2007) describes pit characterization using White Light Interferometry and software analysis (Holme & Lunder, 2007). The program analyses low resolution images to locate and direct the white light interferometer to capture high resolution images that are analysed to find depth, volume and maximum width of pits. This technique is limited to pits that do not experience undercutting and is best utilised to pit initiation and early propagation. This technique generates 3-D experimental data of pits.

2.2.1.12 Analysis of Pit Identification Knowledge

The effectiveness of these non-destructive evaluations is important to operations in harsh marine environments and needs to be understood. These techniques will be used in the design of components to select the best material, manufacturing, and installation practices, and in operations to plan inspection and maintenance scheduling, and in developing models for predicting asset lifecycles (Heerings, Trimborn, & den Herder, 2007).

The referenced work summarized above with respect to pit identification indicates that there is significant information on pit identification techniques available and that they are well understood. New techniques that improve accuracy and reduce human errors are currently in development and will lead to increased confidence in pit identification. The depth of understanding of pit identification can be considered at a ranking of 8. Techniques are available to quantify pitting depth and severity in many marine applications. Further study is ongoing to improve on-line

monitoring of pitting corrosion and to further understand correlation between measured values and pit depth. The breadth understanding of pit identification is determined to be in the mid-range (6). While information is available to assess pitting from many different approaches including laboratory, field and on-line monitoring, there remain many instances where timely, cost effective pit identification techniques are unavailable.

2.2.2 Experimental Methods

The evaluation of pitting behavior is required to fully understand and predict the phenomenon. Determining relationships between many factors including composition, temperature, and environmental conditions is conducted through experiments. Pitting rates determined through experimental methods are generally used in prediction models. Because these rates are used to conduct remaining life assessments, experimental methods need to be conducted such that the results can be extrapolated over longer periods of time.

Many different methods can be used to collect the data required to further understand pitting corrosion. Information can be gained from in-service observation and experimentation, field testing, and laboratory experiments. For many situations, there are standard methods available however; much work has been conducted using generalized corrosion test planning methods that are specific to the situation under review. The method described by Cramer et al. (2005) includes the general 5 step design (Cramer & Jones, 2005):

1. Goal and Objective definition
2. Corrosion Test Design
3. Protocol development
4. Test Engineering
5. Test Modification

These five general steps are used to adapt current standards to unique situation while ensuring the results are recorded, evaluated, and reported in a systematic, repeatable manner.

2.2.2.1 **Standards**

Standards are available to evaluate pitting susceptibility of various materials and environments (ASTM G48, 2011), (ASTM G150, 2010), (ASTM F746, 2009), and (ASTM G61, ASTM G61 Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys, 2009). These standards can be used as a comparative tool to determine the likelihood of pitting in specific circumstances and cannot indicate behavior of materials in service.

ASTM G48, “Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution”,

describes 6 test methods to determine relative pitting and crevice corrosion resistance of stainless steels (ASTM G48, 2011). Methods A, C, and E of this standard deal specifically with pitting corrosion. Method A is a Ferric Chloride Pitting Test and C and E rank materials based on critical pitting temperature (CPT). For this standard, CPT is the temperature at which pitting of a depth of at least 0.025 mm is expected. The results of these methods are used for comparison and ranking of materials in chloride environments. These tests are accelerated and the rate and extent of pitting are not representative of expected field results.

ASTM G-150, the "Standard Test Method for Electrochemical Critical Pitting Temperature Testing of Stainless Steels" (ASTM G150, 2010), includes procedures for determining the potential independent critical pitting temperature (CPT) of stainless steels using electrochemical methods. For this test, CPT is found when the measured current rapidly increases. The onset of pitting above this CPT is visually verified after the test. Again, the standard procedure accelerates corrosion in a way that does not represent any actual service environment.

ASTM G-61, "Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel, or Cobalt-Based Alloys" (ASTM G61, 2009), is used to determine the relative susceptibility of a material to pitting. This is recorded as the potential at which the anodic current increases rapidly. Higher potentials (more noble) are an indication of increased resistance to pitting. This procedure induces corrosion and the results are not intended to indicate the rate of pitting expected in service.

These methods are used to further the understanding of pitting behavior and to assist in determining the effects of change on the resistance of a material to pitting. Siow et al. (2001) used a method similar to ASTM G61 to evaluate the complex effect of alloying and microstructure on pitting (Siow, Song, & Qiu, 2001). They found that the effect of alloying is complex and that the alloying elements may increase or decrease the effects of other alloying elements. They also report that pits started at the ferrite-austenite border and then spread into the austenite and ferrite phases.

It should be noted that there are standardized tests for accelerated corrosion including ASTM B117, “Standard Practice for Operating Salt Spray (Fog) Apparatus” (ASTM B117-11, 2011)and ASTM G85, “Standard Practice for Modified Salt Spray (Fog) Testing” (ASTM G85-11, 2011). Both of these standards allow for increased severity of a corrosive environment to accelerate corrosion. The results from these tests can indicate pitting however; there is limited correlation between field results and these accelerated tests (Acevedo-Hurtado, et al., 2008) .

2.2.2.2 Non-Standard

Experimental methods can also be developed to simulate and evaluate pitting behavior in specific situations and to evaluate pitting resistance changes due to controlled factors. Researchers can adapt accepted standards to tailor methods to these situations.

Studies use accelerated testing to rank materials in terms of their pitting resistance rather than to determine corrosion rates (De-Abreu, Helander, Suarez, Manko, & Clark, 2012). Researchers (Moran, Frankel, & Kim, 2011) and (Lothongkum, Vongbandit, & Nongluck, 2006) have used modified cyclic potentiodynamic polarization to evaluate pitting corrosion resistance and Krakowiak et al. (2002) developed their own methodology to determine the effect of temperature rate change on the critical pitting corrosion temperature (Krakowiak & Darowicki, 2002). They used three electrode measurement vessels with controlled temperature change and determined that the CPT does not depend on temperature change rate in their experimental range.

Researchers from Kushiro National College of Technology and Kitami Institute of Technology in Japan developed an experimental procedure to study the effect of a freeze thaw cycle on pitting of welded austenitic stainless steel (Takahashi, Shibano, Ishitsuka, & Kobayashi, 2012). This procedure was developed to help evaluate structures in coastal regions with severe chloride containing environments. The researchers incorporated the Japanese Industrial Standard (JIS) G 0578 “Method of ferric chloride tests for stainless steels” (JIS G 0578, 2000) and modified the test solution composition and temperature because the environment under investigation was not comparable to standardized tests. The study concluded that pitting corrosion was more severe in the freeze-thaw specimens than in the constant thaw specimens as determined by increased mass

loss. Also, they determined that tensile residual stress is related to accelerated pitting corrosion.

Electrochemical impedance spectroscopy (EIS) is another method that uses applied current to study pitting corrosion. Sorg & Ladwein (2009) used this method to determine the susceptibility of a material to pitting corrosion in the presence of low conductivity electrolytes. They found that EIS allowed for polarization resistance analysis in low conductivity fluids (Sorg & Ladwein, 2009). Jai et al. (2010) used staircase EIS to evaluate pitting in 316 L stainless steel. They found that passive film breakdown was the most likely cause of pitting corrosion (Jia, Du, Li, Yi, & Li, 2011).

2.2.2.3 Field Testing

Field testing is an important method to gather long term information about corrosion in a natural environment. To study pitting in real situations, field testing has been conducted by researchers (Chaves & Melchers, 2012), (Melchers , 2004), and (Phull, 2003). Field testing had helped to demonstrate that while short term testing and accelerated testing are valuable in understanding corrosion, they can be misleading in predicting pitting behavior over the long-term (Chaves & Melchers, 2012) (Acevedo-Hurtado, et al., 2008).

Atmospheric tests are another important method of gathering information and evaluating pitting corrosion in marine environments. ASTM has many relevant standards that can be used in pitting corrosion field testing including (ASTM G33,

2010), (ASTM G50, 2010), and (ASTM B826, 2009). While these standards are not specific to pitting, if the mechanism of corrosion of the material being studied in the tested atmosphere is pitting, they can be used in pitting corrosion studies.

2.2.2.4 Analysis of Experimental Methods Knowledge

Experimental methods to compare pitting resistance of materials are well established and can be successfully modified to accommodate different corrosive environments. This is useful in identifying likely candidates for service applications through relative resistance to a specific environment. Standard laboratory methods for pit evaluation have not been developed to attempt to determine corrosion rates of pitting that can be translated to real life situations. Accelerated corrosion testing is not valid to determine pitting rates in service. Field data has shown that short term testing cannot be relied on to predict long term corrosion behaviour. For these reasons, the experimental methods category is classified as a mid-range depth with a score of 4 and a wide breadth score of 8 due to the prolific application of testing across industries, material types, and corrosive environments.

2.2.3 Pitting Mechanism

One application of experimental methods is to aide in determining the mechanisms involved in pitting behaviour. In marine applications, pitting usually occurs in coated or naturally protected materials. Corrosion resistance in stainless steel is partially due to a naturally occurring passive oxide layer that forms over the surface

of the material. For other types of steel, such as carbon steel, corrosion protection is sometimes due to an applied protective coating. Although these protective layers prevent corrosion over the bulk of an asset, it is where the layer fails or is inconsistent that localized pitting corrosion can occur.

Pitting capitalizes on breaks in the protective layer. A breakdown in the protective layer, either natural or applied, provides a nucleation point for the formation of pits in the presence of an electrolyte containing an aggressive anion (Szklarska-Smialowska, 2005). For marine operations, this ion (Cl^-) is readily available in seawater and marine atmospheres.

According to Schumacher, (Schumacher, 1979) some metals exposed to a corrosive environment will develop pits due to salt particles or other contaminants. Other factors that contribute to pitting including:

- Inclusions
- Discontinuities in protective coating (both natural and applied)
- Surface defects

The mechanism of pitting is not fully understood however most theories look at pitting as a combination of stages. Pitting corrosion damage is identified by Engelhardt et al. (2004) as a three stage event including (Engelhardt & Macdonald, 2004):

Stage 1: Nucleation: in this stage, pits are initiated (nucleated)

Stage 2: Propagation: here, some pits begin to grow

Stage 3: Repassivation: this stage includes pits that cease to continue to grow.

These stages can occur simultaneously leading to large variation in the location, depth, severity, and density of pitting. This contributes to the complexity of predicting pitting rates and to the current view of pitting corrosion as a random process.

2.2.3.1 Nucleation

The nucleation of pits is influenced by surface defects that may be due to manufacturing issues, installation problems, maintenance procedures, and /or environment changes (Baboian, 2005) (Heidersbach, 2011).

The sight of pit initiation (nucleation) can be caused by many different factors:

- Damage to protective oxide layer (chemical or mechanical)
- Environmental factors causing protective layer breakdown
    - Acidity, low dissolved oxygen
    - High chloride concentration
- Damage to applied protective coating
- Poor application of protective coating
- Material structure non uniformity

All of these factors lead to adjacent anode and cathode sites available for corrosion if an electrolyte is present. Pit nucleation sites can be categorized in two different combinations (Roberge P. R., 2008):

Combination 1: Abnormal anodic site surrounded by normal cathodic surface where the anodic sites will corrode.

Combination 2: Abnormal cathodic site surrounded by normal anodic surface where pitting corrosion will occur.

Figure 6 illustrates these two combinations. Combination 1 indicates a higher expected corrosion rate and more severe pits. This is expected due to the difference in surface area of the anode and cathode. The cathode (normal surface) has a much larger surface area than the anode and will corrode the smaller anode quickly and produce deeper pits. This is expected in materials with an applied coating.

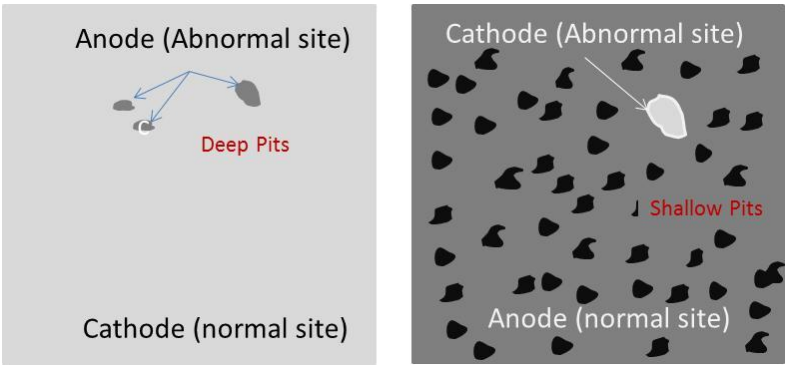

Figure 6: Pit Nucleation Site Combination. (a) Combination 1, abnormal anode, normal cathode. (b) Combination 2, normal anode, abnormal cathode.

Combination 2 can lead to more extensive overall pitting of the surface however this can be a benefit when the abnormal cathodic area is much smaller than the surrounding anodic (normal) surface as pits in this combination tend to be shallow and less likely to extend through the wall thickness. Pits can be seen over the bulk of the metal with only a small area of unaffected local cathode. Roberge (2008) considers this combination to be the most common (Roberge P. R., 2008).

Passive film breakdown

In stainless steel, the breakdown of the passive film provides the site for pit nucleation. These breakdown sites are susceptible to corrosion. Predicting this breakdown is difficult and no generally accepted model has been identified. Further discussion on modeling of pitting can be found in the sections that follow.

Passive films are present on the surface of stainless steels in the presence of oxygen. At low temperatures, a true oxide layer is not formed but a thin passive film is formed and acts as a barrier and provides corrosion resistance (Grubb, DeBold, & Fritz, 2005). This film should be continuous, nonporous, insoluble, and self-healing to fully protect against corrosion. Alloying elements and environmental conditions determine the success of this protection.

In marine applications, hydroxide ions help form the passive film and chloride ions attack the film, causing openings for pit formation. The tug of war between these reactions limits pit initiation (Novak, 2007). If formation of the passive film is the

stronger reaction, the opportunities for pit initiation is reduce; if the breakdown reaction dominates, pitting is encouraged.

The pitting potentios (E_{pit}) is a generally accepted indication of resistance to pitting however there remains uncertainty due to experimental scatter, the dependence of E_{pit} on experimental parameters, and experimental evidence of pit initiation below E_{pit} (Frankel G. , 1998).

Electrochemical studies using cyclic anodic polarization indicate that pits form at a potential above a characteristic potential E_{pit} (Jones, 1996). This has been shown to be valid for both electrically and chemically induced potentials.

The susceptibility of metals and alloys to pitting corrosion can be estimated using polarization curves (Szklarska-Smialowska, 2005) and can be developed through standardized methods discussed in Section 2.2.2.1 (ASTM G61, ASTM G61 Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys, 2009). The curves are used to find pitting potential ***(***E_{pit}***)*** and re-passivation potential (***E_R***). A schematic can be seen in Figure 7:

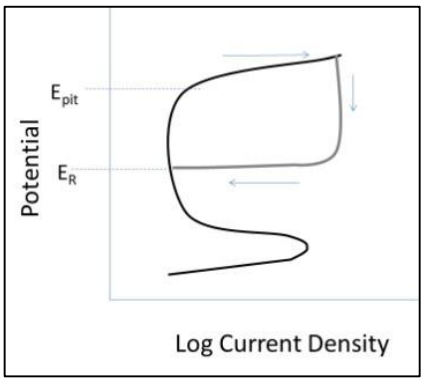

Figure 7: Schematic of anodic polarization curves for a metal immersed in a solution containing aggressive ions. (Szklarska-Smialowska, 2005) (Jones, 1996) (Frankel G. , 2008)

Higher (positive) E_{pit} for a material in a given environment indicates greater resistance to pitting (Szklarska-Smialowska, 2005) (Jones, 1996). If the potential is reduced below E_{pit}, the surface may re-passivate and pit growth can stop. If the potential is between E_{pit} and E_R, pitting is expected (Craig, 1991).

2.2.3.2 Propagation

This stage of pitting is where pits grow and have the potential to increase beyond wall thicknesses and lead to leaks.

For pits to propagate, certain conditions must be met:

1. E_{pit} must be exceeded and remain above E_R
2. An aggressive ion must be present
3. Localized breakdown of passive or applied film

Pits are thought to initiate when the potential of the cell exceeds the pitting potential (E_{pit}) of the material in a given environment and grow (propagate) if the potential remains above the repassivation potential, E_R (Frankel G. , 1998).

There are many theories for the mechanism of pit growth. Jones (1996), in his text book “Principles and Prevention of Corrosion (Jones, 1996) describes pit growth as an autocatalytic process. Within a pit, Fe^{2+} ions attract negative ions (Cl^- in marine applications) and through hydrolysis create a porous $Fe(OH)_2$ cap over the pit. This creates a self-propagating system where the increased acidity in the pit cavity increases corrosion of the steel walls of the pit. Cl^- ions migrate through the cap into the pit and Fe^{2+} migrates out.

2.2.3.3 Repassivation

Pits that continue to grow in stage 2 are the pits that will eventually threaten the integrity of an asset; however, all pits that are initiated (stage 1) and propagate (stage 2) do not always continue to grow. Pits can repassivate and stop growing. This is common in materials that have a naturally produced passive layer such as some stainless steels. In steels that are protected by an applied coating pitting may be stopped by reapplication of a coating. Repassivation can be thought to occur below the E_R.

Work by Novak (Novak, 2007) suggests increased internal resistance of the local cell within the pit is the reason for pit death (repassivation). The author suggests that the increase in resistance may be due to:

1. The pit filling with corrosion products
2. Filming of the cathode that limits reaction.
3. Drying out of the surface (if rewetted, pits may reinitiate and continue to grow)

2.2.3.4 Analysis of Pitting Mechanism knowledge

The above review of work done to understand the mechanism of corrosion illustrates the need for continued study. It is generally accepted that there are three stages to pitting however there is much disagreement in the phenomenon behind each stage. Pits can be initiated in many different ways and the growth of pits can be attributed to different phenomenon. The reasons for pit repassivation are also not well understood. For these reasons, pit mechanism had been assigned a depth score of 3 and a breadth of 3.

2.2.4 Modeling of pitting corrosion rates

The rate of corrosion of pits is an integral part of predicting pitting behaviour and assessing remaining life of assets susceptible to pitting corrosion. The following summarizes the current understanding of pitting corrosion rates observed in the literature.

2.2.4.1 Modeling Pitting Rates in Piping Under Insulation

Developing a model to predict CUI behavior in marine environments is needed to reduce failures, optimize maintenance and inspection schedules and aid in material selection for such applications. Pitting is a key degradation mechanism found in the field and a method for modeling the rate of pitting under insulation is needed.

Recommended Practice by Det Norske Veritas, DNV-RP-G101 (DNV RP-G101, 2002) uses degradation modeling to plan risk-based inspections. This method will be discussed in Section 2.2.2.6. The recommended practice includes a model for corrosion rate of carbon steel under insulation. It describes the rate as normally distributed and is a function of temperature. Table 3 summarises this rate.

This model assumes that if the insulation is wetted by salt water, these rates will apply and if insulation is not wet, there will be no CUI. This model is not specific to pitting and is a general corrosion rate model for CUI in carbon steel. This recommended practice does not include a corrosion rate model for stainless steel under insulation; the effects of CUI for stainless steel are accounted for using a probability of failure (PF) model that is included in Section 2.2.2.5.

Table 3: Corrosion rate (CR) determination for carbon steel under insulation from DNV-RP-G101 (2002)

Temperature (T)	Mean CR (mm/yr)	Standard Deviation (mm/y)	Comment
< -5°C			Probability of failure = 10^{-5}
-5°C to 20°C	Same as 20°C	0.286	May overestimate rate, failures found at low temperatures
20°C to 150°C	0.0067 x T+0.3	0.286	
>150°C			Refer to a specialist

Pitting is an issue under insulation however, no other information was found to indicate studies in this specific situation. As no information was found, the models for pitting corrosion in other situations summarized below may be used as a guide towards the development of a model for pitting rates of assets under insulation.

2.2.4.2 Predicting Pitting Rates

In operation, the depth of pitting is the most important characteristic that needs to be modeled. It is the depth of a pit that will effect containment and structural integrity of pipes and other components in marine environments.

A validated deterministic model for predicting pitting rates has not been found due to the complexity of the contributing factors and the apparently random nature of the process.

One study (Svintradze & Pidaparti, 2010) developed a governing equation for corrosion degradation due to pitting. This model was derived from solid state physics and attempted to model pit radius over time. This model included parameters that the authors were not able to determine and they recommended that further experimental work be conducted to validate their model.

Engelhardt et al. (1997) proposed a method that calculates damage functions for different types of localized corrosion types (pitting, crevice and stress corrosion cracking) (Engelhardt, Urquidi-MacDonald, & MacDonald, A Simplified Method for Estimating Corrosion, 1997). This method is the only one found that allows for environmental conditions that change with time (corrosion potential, temperature, electrolyte composition, etc.). Using the damage function they suggest extrapolating short term experimental data to service life using extreme value statistics. They also argued that damage function analysis is an effective method for predicting future corrosion damage and indicate that updating the model with inspection data will improve the model.

The model depends on understanding four independent functions, the rate of defect nucleation, growth rate of the defect, rate of transition of one kind of defect to another, and the transition of an active pit into a passive pit or the transition of a pit into a crack.

To determine the rate of pit nucleation the point defect model can be used. This model includes external conditions of temperature, pH, metal potential, and halide

ion activity to determine pit nucleation rate. To determine pit growth rate, they use an interpolation equation rather than the simple power law equation $L = At^B$ (Engelhardt, Urquidi-MacDonald, & MacDonald, 1997)

Valor et al.(2007) proposed a stochastic model to simulate pitting corrosion by combining pit initiation (Weibull function) and pit growth (non-homogeneous Markov process) (Valor, Caleyo, Alfonso, Rivas, & Hallen, 2007). They used extreme value statistics (Gumbel distribution) to determine maximum pit depth for extended periods of time. The authors validated their model using published data however; their method has been called into question by the original publisher of the data. Melchers (Melchers, 2007) argued that the model is not appropriate for extrapolation from short term experimental data to long term exposure because of its dependence on the power function for pit depth.

Stochastic models most commonly use extreme value distributions as maximum pit depth to be conservative and prevent leaking.

The Markov chain approach has been used to model pitting corrosion under the assumption that pitting damage is memory-less and current state alone determines future behaviour (Caleyo, Velázquez, Valor, & Hallen, 2009).

Provan et al. (1989) developed a Markov stochastic process to model pit growth with time (Provan & Rodrıguez III, 1989). The system was modeled by a discrete-space, continuous-parameter Markov process. They applied Extreme value statistics to predict the deepest pit and found that if the maximum pit on an area is

in one state (j-1) at time t, then during a time interval (t + Δt), the pit grow to the next state (j) with probability

$$\lambda(j-1)\left[\frac{1+\lambda t}{1+\lambda t^{k}}\right]\Delta t$$ where λ, k are corrosion system dependant and are based on short term experimental data.

Caleyo et al.(2009) used a continuous-time, non-homogenous linear growth Markov process to model external pitting corrosion in underground pipelines (Caleyo, Velázquez, Valor, & Hallen, 2009).

In other work, Melchers has developed a model for corrosion in marine environments (immersion and atmospheric) that shows distinct phases, each with different corrosion rates based on the driving corrosion mechanism (Melchers, 2003) (Melchers, 2004) (Melchers, 2008) (Melchers & Jeffrey, 2008). Figure 8 illustrates this model.

This model suggests that the conventional model for corrosion loss, $C(t)=A\ t^{B}$, is not applicable for the life of the component. The conventional model is based on diffusion of oxygen through increasingly thick corrosion layers and does not take into account changes in corrosion mechanisms with time (Roberge P. R., 2008).

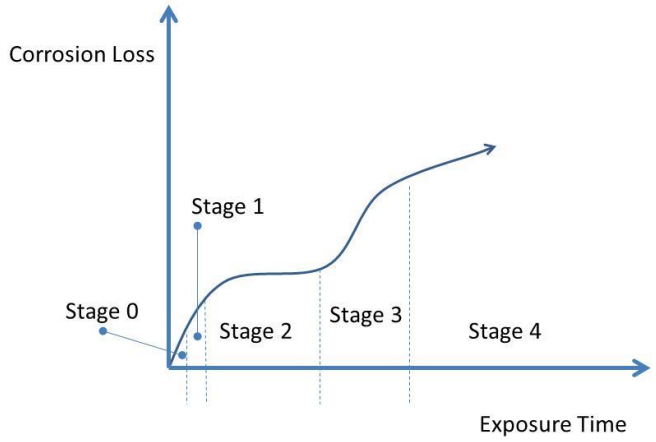

Figure 8: General schematic of model for corrosion loss showing the changing behaviour of the corrosion process as a series of sequential phases adapted from (Melchers, 2003)

Melcher has demonstrated through experimentation that this phenomenological model is applicable to pitting corrosion in marine immersion. His model shows five distinct stages, each with different pitting rate (pit depth/time) based on the driving corrosion mechanism (Melchers, 2004).

In Figure 8, stage 0 is due to water velocity and surface finish, stage 1 is kinetic phase limited by oxygen diffusion through adjacent water, stage 2 is controlled by the rate of oxygen through corrosion product, stage 3 is rapid corrosion under anaerobic conditions, and stage 4 approximates steady state corrosion under anaerobic conditions. Parameters for this model were determined from long-term experimental field data.

2.2.4.3 Analysis of Pitting Rate Prediction Knowledge

As discussed above, there is little agreement on modeling of pitting corrosion behavior in marine applications. Pit depth had been identified by most as the key parameter to describe the rate of pitting and there have been many attempts to model this behavior. The causes of pitting corrosion can affect the rate of corrosion as seen in Figure 8, the more traditional power law model is still used that does not take into consideration fundamental changes in the driving force of corrosion over the long term. Due to this lack of consensus, correlation and validation, the score for pit modeling is low for both depth and breadth at 2.

2.2.5 Prediction of Asset Life (Fitness of Service) under Pitting Attack

Corrosion rates for a particular material in a specific environment can be used to make predictions about the life of an asset. The likelihood that an asset will continue to perform its function can be assessed in a variety of methods. Fitness-for-service (FFS) assessments are a common method to make these assessments. Evaluation of asset life can be made before a component is put into service to assess manufacturing or after to assess in-service damage (Holtam, Baxter, Ashcroft, & Thomson, 2011).

Many studies have predicted asset life or remaining life of components. In this work, we are primarily concerned with prediction of asset life under pitting corrosion attack. In the literature, pit density and maximum pit depth are the most important characteristics needed for assessment of component remaining life.

2.2.5.1 Standards and Recommended Practices

Holtam et al. (2011) surveyed FFS trends in industry to understand the application of FFS across industries (Holtam, Baxter, Ashcroft, & Thomson, 2011). The survey found that API 579-1/ASME FFS-1 standard, “Fitness-for –Service” (API 579, 2007) was the most frequently used standard and that corrosion and erosion damage mechanisms were the most frequent procedures used within any standard.

API 579-1/ASME FFS-1 standard, Fitness-for -Service**,** outlines the method to assess the remaining life of components. For this work, part 6 of this recommended practice is discussed for its applicability to pitting.

Part 6, *Assessment of pitting corrosion*, gives a step by step method to qualify an asset for continued service based on known pitting damage. The assessment is used to determine the course of action for the component in terms of; rerate, repair, or replace.

There are three levels of assessment and each has conditions that govern their applicability. Generally, level 1 assessment is carried out on the simplest components and as complexity increases, more detailed assessments are required (level 2 and level 3). The assessments may also be completed sequentially if a lower level does not produce satisfactory results.

All assessment levels require equipment design data, maintenance and operation history, and material properties.

For level 1 assessment, pit damage is classified by pitting charts to determine the grade of pitting (1-8) and for level 2 a representative site is chosen for assessment with a minimum of 10 pit-couples included.

The level 1 assessment uses maximum pit depth to determine a remaining strength factor that is used to determine if the asset is fit for continued service. If the asset does not pass level 1 assessment, the component can be directly repaired or replaced, or a level 2 or 3 assessment needs to be conducted.

Level 2 assessments determine if there is remaining strength in the component in both the circumferential and longitudinal stress directions. If the component does not pass a level 2 assessment, again the options are to repair, replace or conduct a level 3 assessments.

Level 3 uses numerical methods to assess complex components and indicates if a component is fit for continued service, needs to be replaced, or repaired.

The remaining life of the component can also be estimated using this standard following a maximum allowable working pressure of the undamaged component (MAWP) approach. This assessment uses a pit propagation rate (PPR) to estimate future damage and to estimate MAWP as damage progresses with time. PPR is not specified in the standard but indicates that "… a Pit Propagation Rate should be determined based on the environmental and operating conditions (API 579, 2007, pp. 6-12)

There are other recommended practices to assess fitness for service and asset life available that are not summarized in this work. Some of these standards are summarized in Table 4. This table also includes an assessment of how these standards specifically address pitting corrosion.

Table 4: Select Recommended Practices for FFS assessments including specific methods for addressing pitting corrosion.

Standard/Recommended Practice	Specific Pitting corrosion assessment procedure included	Method for determining pitting rate included
API 579-1/ASME FFS-1: Fitness-for -Service **(API 579, 2007)**	YES	NO
BS 7910 : Guide to methods for assessing the acceptability of flaws in metallic structures **(BS 7910, 2005)**	NO	NO
FITNET: European fitness for service network **(FITNET, 2006)**	NO	NO
ASME B31.G : Manual for determining the remaining strength of corroded pipelines **(ASME B31.G, 2012)**	NO	NO

API 579-1/ASME FFS-1 is the only reviewed standard that specifically addresses pitting corrosion and no standard was found that includes a method for determining the rate of pitting.

Recommended Practice DNV-RP-G101 (DNV RP-G101, 2002) uses degradation modeling to plan inspections. This method is discussed in Section 2.2.6. To predict asset life this recommended practice uses a probability of failure (PF) per unit wall thickness as a function of temperature for local corrosion and stress corrosion cracking. Figure 9 illustrates the method included in DNV-RP-G101 to find the PF for local corrosion under insulation.

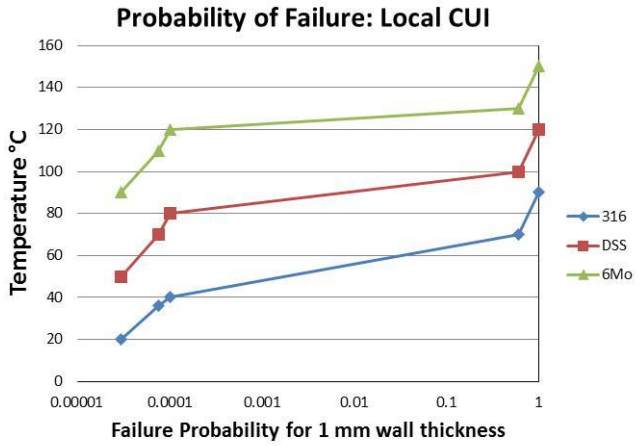

Figure 9: Schematic adapted from DNV-RP-G101 PF for local corrosion of stainless steel under insulation as a function of temperature (DNV RP-G101, 2002).

In addition to the standards discussed above, there are many scholarly works that attempt to predict asset life of a component. As discussed in earlier sections, there is no consensus on modeling of pitting rate. For this reason, statistical models that predict the probability of failure of a component have been developed to minimise the effect of this issue.

Hodges et al (2010) developed an internal system to assess corrosion risk that overcomes the lack of information available in practice. Their method incorporates data from many sources including engineering judgement. This method can then be used to plan monitoring systems and inspection schedules. The result of their work is a semi-quantitative risk assessment that they have shown to be useful to different assets and industries.

Others attempt to understand asset integrity modeling using uncertainty modeling (Thodi, Khan, & Haddara, 2009), (Race, Dawson, Stanley, & Kariyawasam, 2007), and (Akmar Mokh & Ismail, 2011). They found that pitting corrosion was most

closely modeled using type1 extreme value and 3P-Weibull distributions. These models are then updated using Bayes theorem to assess risk to assets in service. They also incorporated inspection data into this model; this allows for the asset risk to be updated with new information and will lead to more realistic assessments of remaining asset life.

Other applications of asset integrity modeling for components susceptible to pitting may be useful to understanding CUI in marine applications.

Race et al. (2007) have developed a corrosion scoring model based on corrosion susceptibility and severity (Race, Dawson, Stanley, & Kariyawasam, 2007). They have developed this method considering three failure modes:

Probability of:

1. Coating failure
2. Cathodic protection failure
3. Corrosion of unprotected pipe in soil environment

The model is developed by finding the probability of failure for each failure mode where:

Probability of failure (PF) = Susceptibility factor x Severity factor

1. Coating failure PF = COATPF
2. Cathodic protection failure PF = CPPF

3. Corrosion of unprotected pipe in soil environment PF = SOILPF

These probability scores were determined through assessment of published data and engineering judgment. Combining all probability of failure scores led to a total failure score (TFS) for the system:

$$TFS = \frac{COATPF + CPPF + SOILPF}{3}$$

The TFS is then fit to known data to determine a corrosion rate based on this score.

For this study (Race, Dawson, Stanley, & Kariyawasam, 2007) the authors found:

Maximum corrosion rate (mm/y) = 1.58×10^{-4} TFS

In another study (Akmar Mokh & Ismail, 2011) the authors used the thinning failure function proposed by Khan et al (Khan, Haddara, & Bhattacharya, 2006) to assess failure of insulated piping. In this analysis, the variables are again assumed to be random, however, their distribution is assumed to be normal and the mean and standard deviation known. The failure probability is found using the following equation

$$pf = \int f_1(x_1)...f_n(x_n)dx_1....dx_n$$

where $f_1(x_1)$ is the probability density function of each variable.

Using FORM to determine a reliability index β that satisfies the failure function and leads to a simplified function for failure probability for each defect. The probability

of failure of the pipeline system can be found using projection operations as follows.

$$pf\,(pipeline) = 1 - \prod (1 - pf_i)$$

The authors assume the defects are mutually exclusive. As this analysis has shown, the behaviour of defects (pits) is complex and interaction and dependence of pits can be reasonably assured making this assumption by the authors questionable.

A case study was used to demonstrate usefulness of the function in assessing asset integrity using a corrosion rate that is assumed to be constant in time. The work by Melcher, (Melchers, 2004), (Melchers, 2008), (Melchers, 2007), (Melchers, 2003), and (Melchers & Jeffrey, 2008), has shown that corrosion behavior can vary significantly depending on the corrosion driving mechanism and that a constant corrosion rate is not always appropriate.

2.2.5.2 Analysis of Asset Life Prediction Knowledge Considering Pitting Corrosion

Asset integrity and fitness for service assessments are readily available and many additional procedures have been developed for specific industries and components. The analysis has shown that there is limited information on corrosion rates included in these methods. It is expected that corrosion rates are developed independently and then used in the analysis. As discussed in previous sections,

there is currently no method for determining reliable long-term corrosion rates. For the purpose of this analysis, the depth of knowledge for this category is considered to be mid-level and is assigned a score of 6. This is due to the variety of different methods found indicating a lack of consensus and the lack of information on corrosion rates. The breadth of this category is considered high and given a score of 8. Fitness for service methods has been well demonstrated to be valid over many industries.

2.2.6 Risk-Based Inspection

Risk-Based Inspection (RBI) is a methodology that develops inspection and maintenance plans based on risk. Risk is defined through analysis of the probability of an incident occurring and the severity of the consequences if an incident does occur. Using a risk-based inspection helps to focus inspection resources on key areas, evaluate the system wide risk against an operator set risk acceptance criteria, and develop optimal methods for inspection and monitoring (DNV RP-G101, 2002).

2.2.6.1 Standard and Recommended Practices for RBI

The American Petroleum Institute (API) developed two recommended practices (RP) to address RBI:

1. API Recommended Practice 580: Risk-Based Inspection (API RP580, 2009)

2. API Recommended Practice 581: Risk-Based Inspection Technology (API RP 581, 2008)

API 580 deals with defining RBI and instructing users on how to implement and sustain an RBI program. API 581 gives more specific procedures to develop an RBI program and to provide quantitative methods to assess overall plant risk. These two methods are intended to be used together and will be discussed together for this work.

API 580 defines terms and explains the basic concept of developing an RBI including overview of risk analysis, key elements of RBI programs, establishing boundaries, and data and information collection. It also introduces damage mechanisms and failure modes. These include corrosion, cracking, and metallurgical damage. Section 9.1.1 of API 580 lists general steps for identifying possible damage mechanisms. Once possible mechanisms are identified, section 9.3 of API 580 describes how to assign an associated failure mode. These failure modes can include modes such as pinhole leaks, large leaks, or brittle fracture.

This information is used to complete a probability analysis. A general method for assessing probability of failure (PF) is discussed including qualitative and quantitative methods. Qualitative assessments are based on engineering judgement and then a description (high, medium, low or 0.1 to 0.01 times per year) is assigned. There are numerous quantitative approaches to PF indicated. Using

probability shown as a distribution is one option; using manufacturer failure data is another.

To determine PF, API 580 lists the two main considerations; damage mechanism and rates, and the effectiveness of the inspection program. The steps to analyse these effects on PF are listed in the RP and summarized here (API RP580, 2009):

1. Identify active/credible damage
2. Find damage susceptibility and rate
3. Qualify inspection effectiveness
4. Determine probability that the damage tolerance will be overcome.

Methods for determining these steps are generally discussed in API 580 and more in-depth in API 581 (API RP 581, 2008). API 581 instructs a user on the calculations required to determine a PF for a component or system under study. API assesses PF as a combination of a generic failure frequency, a damage factor, and a management system factor.

The generic failure frequency is the basis of this assessment. It was set for different component types based on representative values from industry failure data. This failure rate is a baseline value before any damage occurs. The damage factor is applied to this baseline for each specific component and the management system factor is applied to all equipment.

Damage factors are determined by specific damage mechanisms. API 581 includes methods for determining damage factors for:

- Thinning (both general and local)
- Component Linings
- External Damage
- Internal Stress Corrosion Cracking
- High Temperature Hydrogen Attack
- Mechanical Fatigue (Piping Only)
- Brittle Fracture

The consequence of failure (CF) is then described and techniques for assessing introduced in RP API 580 (API RP580, 2009). These consequences are categorized as: safety and health impacts, environmental impacts, or economic impacts. Quantitative and qualitative techniques are introduced and can be measured in terms of safety or cost. API 581 includes methodologies for two levels of analysis. Level 1 analysis is a simplified method of evaluating the consequence of release of a limited number of fluids. This method includes determination of important system characteristics such as release rate, release hole size selection and flammable and explosive consequences.

Level 2 CF assessment provides a more detailed procedure for calculation. This analysis is used when the assumptions of the simplified Level 1 assessment are not valid. An example of this situation given in the RP is when stored fluid is close to its critical point and the ideal gas assumption is invalid.

API 580 next generally discusses the risk assessment and management techniques. This section combines PF and CF to determine the risk. Risk = Probability (PF) x Consequence (CF).

API 580 gives information on prioritizing and evaluating acceptable risk and, using examples, demonstrates risk calculations and risk rankings. Once a risk tolerance is developed, the RP gives guidance on how to manage risks that are above the tolerance. Methods such as decommissioning, condition monitoring, and probability mitigation are discussed as ways to manage and reduce risk.

API 580 also gives information on reducing uncertainty in risk assessments through inspections. If damage mechanisms and rates of damage are assessed through inspection and then acted on, these methods can reduce PF and thus reduce overall risk.

API 581 again gives more detail and includes procedures for calculating risk. The RP includes equations for both area based risk and financial based risk.

The results of the risk assessment serve as a basis for developing the inspection plan. API 580 advises that the following be included in inspection procedure development:

- Risk criteria and ranking
- Risk drivers
- Asset history
- Number and results of inspections
- Type and effectiveness of inspections
- Equipment in similar service and remaining life

The type of inspection also plays a key role determining risk. Both API 580 (API RP580, 2009) and 581 (API RP 581, 2008) indicate that there are many factors that affect the risk. Some of these are; frequency of inspection, coverage of inspection, tools and techniques, procedures and practices, and inspection type (internal, on-stream, or external).

API 581 includes specific information on different types of components that may be included in RBI and gives specific advice on following the procedure for each. These components are: pressure vessels and piping, atmospheric storage tanks, pressure relief devices, and heat exchanger tube bundles.

API 580 and 581 do not contain specific sections on pitting corrosion. Pitting is mentioned throughout as a damage mechanism and API 581 indicates that damage rates are increased over general corrosion rates due to pitting for many situations.

- “These rates are 10 times the general corrosion rates to account for localized pitting corrosion” (API RP 581, 2008, pp. 2.B-13)

- ” As a rule of thumb for carbon steel, the pitting rate is a factor of 5 to 10 times the coupon general corrosion rate, (calculated by weight loss).” (API RP 581, 2008, pp. 2.B-98)

DNV-RP_G101 “Risk Based Inspection of Offshore Topsides Static Mechanical Equipment” (DNV RP-G101, 2002) is another example of RBI recommended practice (RP). It describes the methodology for developing a RBI in an offshore production facility. This RP begins with a risk screening to categorize equipment into high, medium, or low risk. The second part of the process is a detailed quantitative assessment of higher risk areas.

The RP includes a guide to the screening process and recommends that this qualitative analysis be carried out by qualified knowledgeable personnel. This guide allows the assessment team to use engineering judgement to identify the consequence and probability (and thus the risk) as high or low for each component or system (DNV RP-G101, 2002). Those components/systems that include a high rating for consequence and probability are further assessed in the detailed analysis. The RP indicates that if there is any question to the rating (high or low) the component/system should be included for further detailed study. Items that are found to have low or medium risk are followed up with maintenance activities and not considered further in the RBI methodology.

The detailed analysis calculates inspection schedules and techniques based on identified degradation mechanisms and current state of damage. This analysis aims to ensure that risk levels do not exceed a pre-determined acceptable risk limit.

This RP gives methods for determining the probability of failure (PF) and consequence of failure (CF) and illustrates the methods for combining to determine risk. Consequence modeling can be based on other analysis (quantitative risk analysis (QRA) or risk assessment methods (RAM)) but the RP also includes simplified methods to assess consequences. Event trees are recommended to identify possible consequence and to determine the CF. The practice separates consequence modeling into ignited and un-ignited consequences and outlines each in terms of personal safety, economic consequences, and environmental consequences.

Probability of failure modeling assesses the likelihood degradation mechanisms, the current PF and determines the PF as it changes with time. This PF will establish inspection intervals. The PF limit is determined from the acceptable risk limit and the CF.

Degradation mechanisms are identified as either an insignificant model, a susceptibility model, or a rate model. An insignificant model is used on specific material/fluid combinations and is considered to be fixed at PF = 10^{-5} /year. Inspection is considered irrelevant for this model (DNV RP-G101, 2002). The

susceptibility model determines PF based on operating conditions. This model is considered to be constant over time for given conditions. Inspection can be used to monitor process parameters. Rate models indicate that damage increases with time. Appendix C of DNV RP G101 includes typical material/fluid combinations and gives methods for determining PF for these situations. Two CUI models were discussed in sections 2.2.4.2.and 2.2.5.1. Other models described include CO_2 model, microbial corrosion, corrosion based on water characteristics, and atmospheric corrosion. More detailed modeling of damage rates is suggested and probabilistic methods are suggested to obtain more accurate results.

Results from all analysis are combined and inspection is carried out to keep the risk of failure below the risk tolerance limit.

The above summarised recommended practices have been used as a guide or adapted by many researchers (Khan, Haddara, & Bhattacharya, 2006), (Khalifa, Khan, & Haddara, 2012)]. These works build on established procedure to improve these practices, increase safety and reduce cost.

Two state functions were developed by Khan et al. (Khan, Haddara, & Bhattacharya, 2006) to describe material degradation. The first is for thinning of carbon steel and copper piping that measures the resistance of the material to applied stress.

$$g_t = S\left(1 - \frac{C \times \Delta t}{d}\right) - \left(\frac{P \times D}{2 \times d}\right)$$

where

S= Material Strength

C = corrosion rate

Δt = time increment

d = material thickness

P = operating pressure

D = diameter of the component,

A state function for stress corrosion cracking was also developed based on Paris's crack growth law (Khan, Haddara, & Bhattacharya, 2006).

$$g_c = K_{IC} - Y\left(\frac{P \times D}{2 \times d} + S\right)\sqrt{\pi\left(\frac{C_{cr}\Delta t^n}{R_{l/a}}\right)}$$

where

K_{IC} = material fracture toughness,

Y =dimensionless geometric factor,

S = residual stress,

C_{cr} = crack growth rate

$R_{l/a}$= crack to length to-depth ratio

The variables in the above models (S, C, P, K_{IC}, Y, P, A) have uncertainty and are considered to be random, making the material degradation process stochastic. These random variables are assumed to be independent and exponentially distributed leading to a gamma distributed process (Khan, Haddara, & Bhattacharya, 2006). Corrosion rate for the thinning model is assumed to be a linear function with time allowing the shape parameter (α) of the gamma distribution to become $\alpha_o t$. This leads to a failure distribution function for cumulative material degradation.

$f_{X(t)}(x) = \frac{\beta^{\alpha_o t}}{\Gamma(\alpha_o t)}(x)^{\alpha_o t-1}e^{-\beta x}$ for x > 0.

This function is then used for inspection updating using new inspection data and Bayesian updating (Khan, Haddara, & Bhattacharya, 2006).

Datla et al. (2008) introduced a probabilistic model of steam generator tube pitting corrosion based on inspection data from a nuclear generating station (Datla, Jyrkama, & Pandey, 2008). A stochastic non-homogeneous Poisson process with pit size as a random variable was used. Their model was based on inspection data of pits that were greater than 50% of thickness.

Intensity function (Non-homogenous Poisson process):

$\lambda(t) = \alpha t^{\beta-1}$

Expected number of pits (Poisson process):

$E[N(t)] = \Lambda(t) = \frac{\alpha}{\beta} t^{\beta}$ α = scale parameter, β = shape parameter

Pit depth distribution (Generalized Pareto Distribution):

$$F_x(x) = 1 - \left(1 - \xi \frac{x - \mu}{\sigma}\right)^{1/\xi}$$ σ = scale parameter, ζ = shape parameter

Extreme pit depth distribution using extreme value theory:

$$F_Y(z) = \exp(-\Lambda_z(t))$$

Inspection data was used to estimate parameters (α, β, λ, ξ, σ, μ)

In other works, Khalifa et al. (2012) describe a methodology used to develop a prediction tool to estimate the inspection sample size needed to determine the maximum localized corrosion depth of a process population (Khalifa, Khan, & Haddara, 2012). As inspection of all component area is not feasible, inspecting limited number of sites may be necessary. To ensure the data collected from limited inspections represents the behavior of the entire system, the correct number of samples needs to be inspected. They developed a new method to determine the required sample size to assess localized corrosion. This method assumes that collected data is independent, has negligible measurement error,

and follows the Grumbel extreme value distribution (Khalifa, Khan, & Haddara, 2012).

The method first divides the process under investigation into corrosion circuits. Each circuit includes components of the same material that are subjected to the same environment. The expectation is that areas in each corrosion circuit will experience the same degradation mechanisms.

The new equation to determine sample size needed to find the maximum localized corrosion was then demonstrated through a case study. Inspection data was used and a sample size determined using the methodology. This sample size was similar to that predicted by the proposed equation.

2.2.6.2 Analysis of RBI using pitting corrosion rate modeling knowledge

Risk-based inspection is well documented and is becoming more and more standard practice in industry. Methodologies are available to guide users through probability and consequence modeling. The recommended practices examined here indicate a well-established procedure for RBI. The RP reviewed include simplified methods for probability and consequence modeling. A need for precise modeling has been identified and the above papers indicate that this work is ongoing. There remains little information on probability modeling for pitting corrosion in general and less for pitting corrosion under insulation.

The depth of understanding of RBI is considered high at 7 as the RBI procedures are well established and standards exist to guide in RBI development. It is the PF elements needed for RBIs that need to be further studied to increase accuracy. Pitting corrosion needs to be incorporated more directly and specifically. The breadth of understanding of this is considered mid-range at 6 as there are many standards used by different industries and there is limited consensus on these methods.

2.3 Analysis and Discussion

2.3.1 Current State of Pitting Corrosion Knowledge

Earlier sections show that while we do understand a lot about pitting corrosion, there are still many aspects of this degradation that are relatively unknown or less known. Figure 10 summarises the assigned depth and breadth rating for the understanding of pitting corrosion in marine applications.

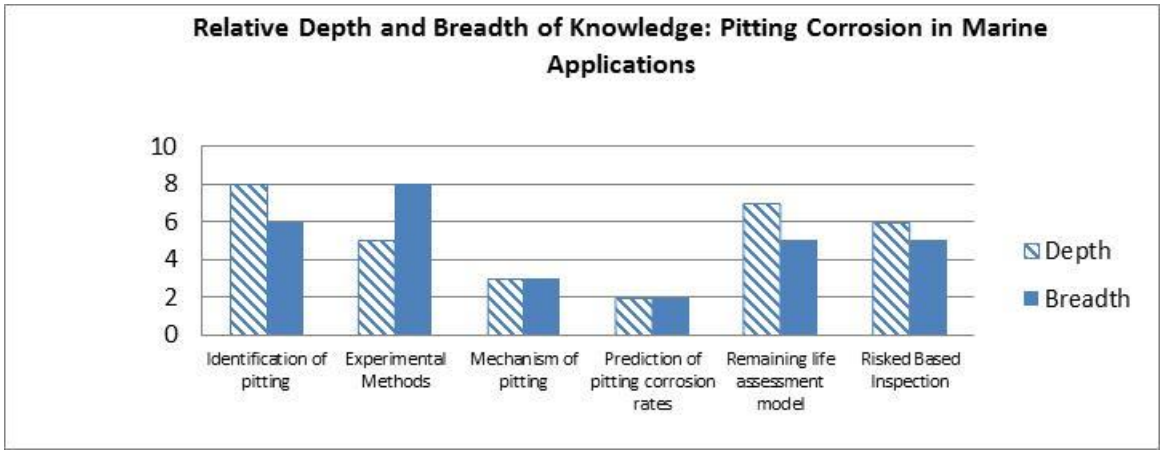

Figure 10: Relative Depth and Breadth of Knowledge: Pitting Corrosion in Marine Applications

This graph clearly shows that the categories that need the most work to enhance our understanding of pitting corrosion are i) the mechanism of pitting and ii) the prediction of pitting corrosion

The depth of knowledge of pitting corrosion modeling is significantly smaller than the other pitting categories analysed. This lack of knowledge is limiting because as shown in sections 2.2.5 and 2.2.6, pitting rate modeling is key to making accurate and reliable assessments. This is essential to improve safety and lower costs through FFS and RBI inspections.

Understanding the mechanism of pitting is also important as increased understanding of the phenomenon will make modeling more realistic. The methods described in section 2.2.2 can be adapted along with the identification techniques described in section 2.2.1 to allow for more research and data collection that will ultimately strengthen our understanding of all categories. These relationships are illustrated in Figure 11 below.

This figure illustrates the interdependence of the six analysed categories. Pitting identification and experimental methods to study pitting are used to further understand and define pitting mechanism.

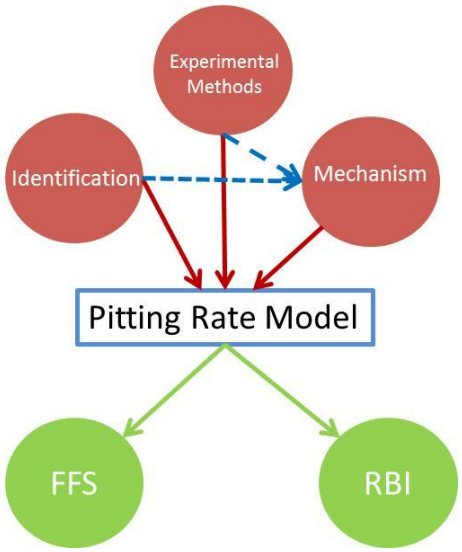

Figure 11: Relationship between pitting corrosion categories

All three of these categories are needed to develop a pitting rate model. This model will then be incorporated into FFS and RBI analysis to improve safety and reduce costs in marine operations.

2.3.2 Pitting Under Insulation

Review of current models available for pipe failure due to corrosion and for corrosion rate has shown that there is no model available that to help model corrosion rates for piping systems under insulation in marine environments.

There are models available that may predict the failure rate of insulated pipes once a precise model of CUI corrosion rate is known.

There are models of corrosion rate available for other environments. These models indicate the importance of different variables that play a critical role in CUI modeling and thus will be used in failure model development.

2.3.3 Future Direction

The development of a corrosion rate model for CUI in offshore environments can only be developed when the variables that affect this type of corrosion are understood and the interactions between variables determined. The following fault tree shown in Figure 12 is used to help identify the base causes of CUI to begin modeling corrosion type for the purpose of fitness for service, RBI and failure modelling.

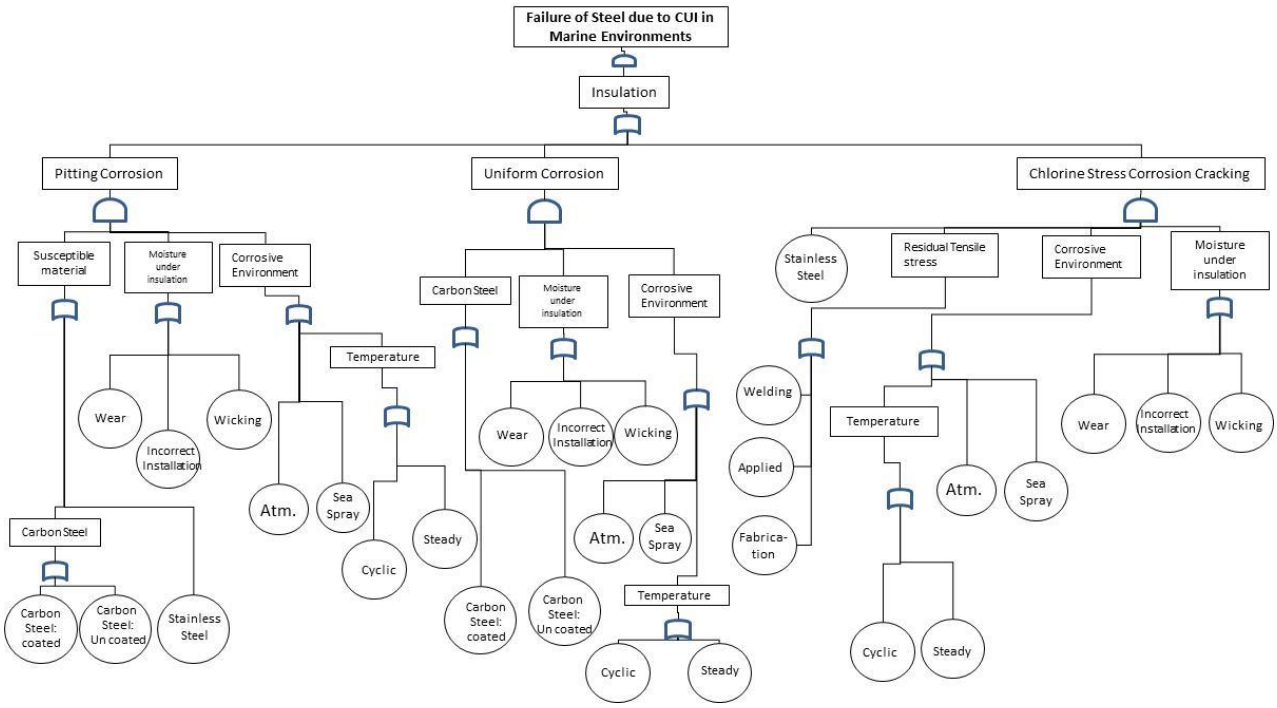

Figure 12: Fault tree of CUI of Steel in Marine Environments (NOTE: Atm. = Atmosphere)

Some of the important causes of CUI in marine environments that need to be studied for their effect on corrosion rates have been identified. These include:

1. Predicting moisture penetration under insulation including:

- Wicking properties of insulation
- Degradation of insulation over time
- Installation issues (Human Factors)

2. Effect of the moisture capturing:
    - Time of wetness (TOW)
    - Chloride concentration [Cl]
    - Sulfur dioxide concentration [SO_2]
    - Rainfall amount
3. Effects of cyclic temperatures
4. Stress induced on stainless steel components.

Bacterial corrosion as a factor for long term corrosion in marine atmospheres was introduced by Melcher in (Melchers, 2004) and (Melchers & Jeffrey, 2008). Bacterial corrosion is sometimes called microbiological influenced corrosion (MIB). No published research is found that investigates this specific corrosion type under insulation. Further study is needed to determine if MIB is a factor along with pitting, uniform and stress corrosion cracking for CUI.

Further research and testing is needed to determine interactions of different parameters and to develop a corrosion rate model for CUI that can be used to predict reliability and fitness-for-service in marine environments.

2.3.4 Research Direction

To begin developing a model for CUI that includes pitting corrosion new field experiment set-up is to be developed. This is important to better understand mechanisms of pitting under insulation and to link this data to engineering design and analysis.

Long term, periodic data collection is needed to determine corrosion rates under insulation. This data is not available from in-situ monitoring in industry due to issues with insulation removal, inspection techniques, and available resources. No field studies have been conducted to attempt to evaluate CUI in marine atmospheric conditions outside of a laboratory.

Most corrosion rates currently used in predictive models are based on short term laboratory corrosion data and no physical justification for the typical power function relationship is known (Melchers, 2004) (Engelhardt & Macdonald, 2004).

To generate long term data, field testing is suggested. This would allow the collection of relevant environmental data and understanding of degradation

mechanisms and corrosion rates. This would also create an opportunity to develop new inspection techniques to help determine pitting rates from on-line monitoring.

Field data could also be used to develop accelerated lab scale testing to further understand the long term phenomenon and to simulate long term exposure at specific environments and develop a pitting rate model.

2.4 Conclusion

This paper has summarised six categories of pitting corrosion and determined the state of understanding for each. It was found that the depth of knowledge of pitting corrosion rate modeling and pitting mechanism are significantly less than the other pitting categories analysed.

From this work the following conclusions indicating the current state of knowledge can be made:

- There is significant information available on pit identification techniques and that these techniques are well understood.
- Well established experimental methods are available to compare pitting resistance of materials.
- It is generally accepted that there are three stages to pitting.
- Pits can be initiated in many different ways and the growth of pits can be attributed to different phenomenon.

- Pit depth has been identified as the key parameter to describe pitting rate.
- Asset integrity and fitness for service (FFS) assessments are readily available and many additional procedures have been developed for specific industries and components.
- Risk-based inspection (RBI) is well documented and is becoming standard practice in industry.
- Reviewed RBI recommended practices include simplified methods for probability and consequence modeling.

Through this analysis, the following conclusions indicating the need for further study can be made:

- Standard laboratory methods that accurately determine pitting rate are not available.
- Field data has shown that short term testing cannot be relied on to predict long term corrosion.
- There is no consensus in the phenomenon of each of the three stages of pitting.
- The reasons for pit repassivation are also not well understood.
- There is little agreement on modeling of pitting corrosion rate.
- No FFS Assessment found includes a method for determining pitting rate.

- Little information on probability modeling for pitting corrosion in general is available; less for pitting corrosion under insulation
- Categories that need the most work to complete understanding of pitting corrosion are the mechanism of pitting and the prediction of pitting corrosion.
- Pitting models are needed for more accurate FFS and RBI assessments
- New experimental methods are needed to develop additional information on pitting.
- New inspection techniques could help determine pitting rates from on-line monitoring

2.5 References

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3.0 Experimental Design to study Corrosion Under Insulation in Harsh Marine Environments

Preface

A version of this paper was published in in the Journal of Loss Prevention in the Process Industries. Susan Caines is the primary author for this work. Co-authors for this manuscript include Dr. Faisal Khan, Dr. John Shirokoff, and Dr. Wei Qiu. The primary author developed the conceptual model, the design of experiments and prepared the first draft of the manuscript. The co-author Faisal Khan helped in developing the concept, the experimental setup, and contributed in preparing, reviewing and revising the manuscript. The co-authors Dr. John Shirokoff, and Dr. Wei Qiu contributed through support in the development and improvement of the design and assisted in reviewing and revising the manuscript.

Minor editing of the published paper was completed to conform to formatting and to correct errors.

Abstract

Corrosion Under Insulation (CUI) is a serious issue in harsh marine environments. Corrosion damage can have catastrophic effects on health and safety, asset integrity, the environment, and productivity if it is not detected and managed early. Limited information is available for CUI in marine environments. To overcome this issue, three types of corrosion tests are proposed: Determination of the effect of environmental factors on CUI using laboratory simulation, field testing, and

accelerated marine atmosphere testing for CUI. This paper describes the methodology for developing statistically significant data to evaluate CUI in harsh marine field conditions, develop an accelerated laboratory test procedure to simulate CUI, develop a model of CUI rate, and develop risk-based remaining life assessment model for assets under CUI attack.

3.1 Introduction

Corrosion under insulation (CUI) is a serious issue in harsh northern marine environments. This type of damage can have catastrophic effects on asset integrity, production losses, health and safety, and the environment in the offshore industry.

CUI is an issue in chemical and petroleum industries and work has been done to understand and combat this issue in onshore operations (Frudge, 2008; Simpson, 2007; Fitzgerald et al, 2003). ExxonMobil Chemical presented a study to European Federation of Corrosion in September 2003 indicating that the highest incidence of leaks in the refining and chemical industries are due to CUI (Winnik, 2003). Between 40% and 60% of piping maintenance costs are related to CUI (Winnik, 2003). This issue becomes more severe in marine operations. While there has been work done to try and understand the causes of CUI onshore, there has not been as much work done on understanding the issue in offshore environments. CUI was identified by industry experts as the number one issue of corrosion at the Corrosion Workshop held in St. John's, NL (Marine Corrosion Workshop, 2012).

Insulation of pipes in the offshore industry is necessary to control processes, conserve energy, and to protect personnel. This insulation is required; however its increased use has contributed to the ongoing and costly problem of CUI (Delahunt, 2003). Insulation over pipes creates spaces and crevices where moisture collects and can remain in contact with the pipe. Figure 13 illustrates this situation. It is in this annular space that corrosion is expected to occur.

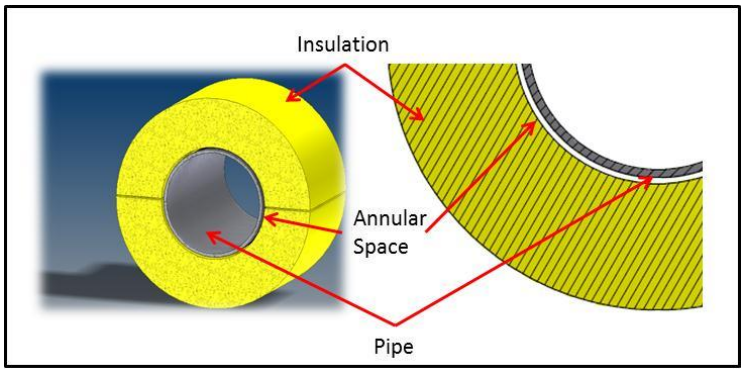

Figure 13: Illustration of annular space between pipe surface and insulation where corrosion is anticipated.

Due to restrictive access, CUI is difficult to monitor and degradation can continue until failure. Operating insulated systems in harsh marine environments is expected to lead to an increase in corrosion failure if effective inspection and maintenance plans are not implemented. CUI is difficult to detect because corrosion occurs under the insulation, preventing detailed inspection without the costly and time consuming task of insulation removal. There are non-destructive testing and evaluation methods available that can indicate issues without the removal of pipe insulation and include ultrasonic and radiographic techniques. These methods can indicate pipe wall thickness change however they cannot be relied upon to give detailed or definitive corrosion loss data. Standard inspection

techniques and recommended practices are detailed in industry standards such as ASTM Standard G46 (ASTM G46, 2005) that detail how to use non-destructive methods to inspect for pitting corrosion and NACE standard practice “Control of Corrosion Under Thermal Insulation and Fireproofing Materials—A Systems Approach” describes inspection and maintenance planning to combat CUI (NACE International, 2010). Risk based inspections (RBI) are also commonly used in industry to develop inspection plans to detect CUI (DNV RP-G101, 2002) (API RP 580, 2009), (API RP 581, 2008). Another resource for combating CUI is the European Federation of Corrosion Publications number 55 edited by S. Winnik, “Corrosion-Under-Insulation (CUI) Guidelines” (Winnik 2008).

Short term, periodic data collection is needed to determine corrosion rates under insulation. This data is not available from in-situ monitoring in industry due to the cost of insulation removal. No studies have been conducted to attempt to evaluate CUI in harsh marine conditions outside of a laboratory. Corrosion rates currently used in predictive models are based on short term laboratory corrosion data (Klassen & Roberge, 2003, Engelhardt, Urquidi-Macdonald, & Macdonald, 1997, Engelhardt & Macdonald, 2004). In addition, there is no effort made to update corrosion rates based on the inspection data. A recent review by Caines et al. (2013) illustrates this point (Caines, Khan & Shirokoff, 2013). The authors found that there is no standardised method to determine pitting rates, that there is limited agreement between long term pitting behaviour and current accelerated laboratory

testing, and that corrosion rate modeling is needed to improve fitness for service and risk based inspection applications.

An understanding of the contributing factors of CUI and how these factors are associated can make the expected behaviour predictable. Developing a model to predict CUI behaviour in marine environments is needed to reduce failure probabilities, optimize maintenance and inspection schedules and aid in material selection for this type of application.

A review of available models for pipe failure due to corrosion and for corrosion rate has shown that there is no model available that predicts corrosion rates for piping systems under insulation in marine environments. Only one failure model that attempts to predict failure probability of a pipe system due to CUI was found (Mokhtar & Ismail, 2011). It utilises a corrosion rate that is assumed to be constant with time. Work by Melcher (2003, 2004) has shown that corrosion behaviour can vary significantly depending on the driving corrosion mechanism and is not linear with time (Melchers, 2003, Melchers, 2004). If a more accurate corrosion rate model is developed for CUI in marine applications, it is possible that a failure model could be developed to predict the probability of CUI, which would assist in developing effective inspection and maintenance plans.

Preliminary research has highlighted a gap in knowledge for predicting CUI in harsh marine environments. This paper proposes research tasks that attempt to fill this gap and lead to better models for predicting CUI in offshore applications.

To do this, three stages of experimental work are needed on the typical offshore steel/insulation couple of low temperature carbon steel (LTCS) under thermal insulation.

Stage 1. A field test to capture long term data on CUI in harsh marine environments. This stage of experimentation is conducted in a natural environment on the coast of Newfoundland.

Stage 2. A laboratory test to characterise CUI to determine factor interaction and affects.

Stage 3. A laboratory test to simulate and accelerate CUI using data collected during the first year of experimentation in the natural setting (Stage 1).

From this three stage method, unique data is generated using inspection, mass loss and electrochemical noise measurements. The data is used to develop a CUI prediction model, damage function, and improved fitness for service and risk assessment methodologies.

Similar methodology has been proposed by Srinivasan et al. (2013) to develop a predictive methodology to combat the effects of wet insulation on CUI (Srinivasan et al., 2013). They proposed a two-step plan similar to Stages 2 and 3 to first characterize the CUI behaviour followed by a more detailed laboratory study. To develop these test procedures and to generate statistically significant results, the design of experimental methodology was implemented for each test regime. The results of this study are presented here.

3.2 Expectations

It is expected that CUI develops over time during these experiments. The type or mechanism of corrosion under insulation is not always known and as such many types of corrosion are possible for LTCS in a marine environment. Uniform Corrosion, Pitting Corrosion, Chloride Stress Corrosion Cracking (CSCC), and Microbial Influenced Corrosion (MIC) are the most common types of corrosion expected. Information regarding these mechanisms is well covered in literature and briefly summarized below.

Uniform Corrosion

Uniform corrosion is the degradation of a metal over all areas exposed to the environment. It is a continuous reaction between anodes and cathodes over the exposed surface that leads to the relatively uniform loss of metal at the exposed surface (Davis, 2000). Uniform corrosion is generally more predictable because the corrosion occurs over the entire area and is easier to measure (Buschow, et al., 2011) and predict. Materials, such as carbon steel, that do not form a natural passivation layer are more susceptible to this type of corrosion. Protective coatings are often used to combat uniform corrosion. This method can successfully protect assets from uniform corrosion; however, any break in the protective coating can increase the likelihood of localized corrosion like pitting, leading to unexpected catastrophic failure of process components.

Pitting Corrosion

Pitting is the most common type of localized corrosion (Roberge, 2008). It is a form of corrosion where the degradation of the material is localized to small areas rather than over the entire surface uniformly. According to Schumacher (1979) some metals exposed to a corrosive environment will develop pits due to salt particles or other contaminants. Other factors can contribute to pitting including:

- Inclusions
- Discontinuities in protective coating (both natural and applied)
- Surface defects

Materials most likely to develop pits are generally coated or naturally protected. Pitting capitalizes on breaks in the materials protective layer where an electrochemical cell can be formed and pits are initiated. In marine applications, pitting can be seen in stainless steel and on coated carbon steels.

Stress corrosion cracking

Stress corrosion cracking is an issue in many industries and environments. All forms of SCC depend on the presence of three factors as shown in Figure 15 :

1. A susceptible material

2. Residual or applied tensile stress
3. A corrosive environment

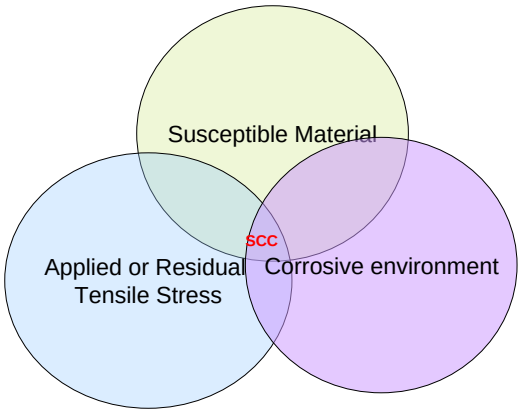

Figure 14: Requirements for SCC

There are many theories to explain the causes of crack growth in SCC. Two theories discussed in literature that describe the controlling factor of crack growth are:

1. Stress intensification at base (fracture mechanics) (Wei, 2010)
2. Enhanced electrochemical conditions. (Shehata et al., 2007)

SCC under insulation is an issue in marine environments ((Delahunt, 2003) ((Ed) Winnik, 2008)). Babakr & Al-Subai (2006) discuss two case studies involving SCC under insulation in process piping. They found that accumulation of chloride on offshore piping with time contributes to the creation of a SCC susceptible environment (Babakr & Al-Subai, 2006).

Microbial Influenced Corrosion (MIC)

Microorganisms including bacteria are found in sea water and these organisms can contribute to material degradation. This degradation mechanism is termed Microbial Influenced Corrosion (MIC). Biofilms can form on the surface of marine structures and can influence corrosion rates, initiate corrosion, or change the mode of corrosion (Duan et al., 2008). The formation of a biofilm does not guarantee any effect on corrosion or on CUI particularly, however, in the marine environment; it is a possible mechanism that must be monitored.

3.3 Methodology

The goal of this work is to understand what effect time, temperature (internal and external pipe), chloride content, time of wetness (TOW[1]) and possible re-insulation have on the corrosion behaviour of low temperature carbon steel (LTCS) under insulation. Low temperature carbon steels are used in applications that require sustained toughness at temperatures as low as -50 °C (Brady, 2002).

This experiment will help determine the time to corrosion, corrosion rates, and types of corrosion. This combination is typical in harsh environment operations. A typical coating system is included as a factor in the experimental design allowing for comparison of protected and unprotected systems. This coating is chosen through consultation with industry experts to ensure the best representative coating is used.

[1] Time of wetness (Relative humidity): TOW is determined when relative humidity is greater than 80 percent at a temperature greater than 0°C (Roberge, 2008).

Another goal of this work is to determine if a similar phenomenological model for corrosion can be seen for CUI corresponding to the work conducted by Melchers (Melchers, 2003; Melchers, 2004; Melchers, 2008). He developed a model for corrosion in marine environments (immersion and atmospheric) that shows distinct phases, each with different corrosion rates based on the different driving mechanism. Figure 15 illustrates this general trend.

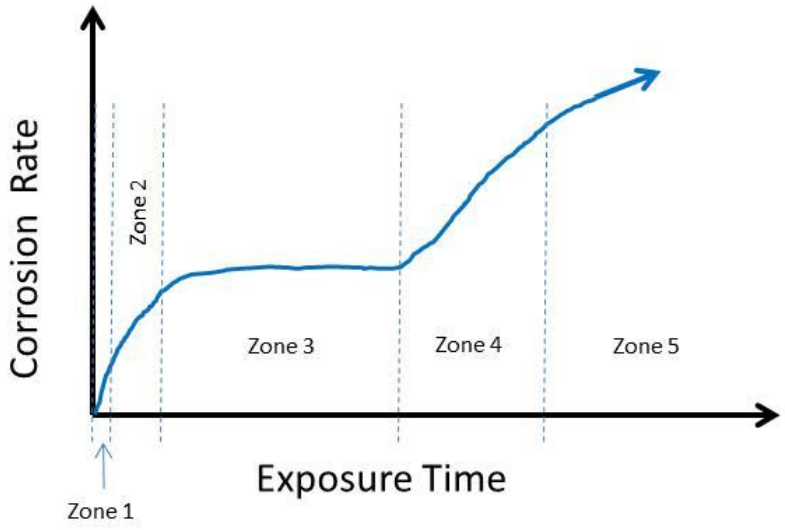

Figure 15: Overall model by Melcher for corrosion loss showing the changing behaviour of the corrosion process as a series of phases (Melchers, 2003; Melchers, 2004; Melchers, 2008)

This model suggests that the conventional model for corrosion loss, $C(t) = A\ t^B$, is not applicable for the life of the component. The conventional model is based on diffusion of oxygen through increasingly thick corrosion layers. It does not take into account changes in corrosion mechanisms with time (Roberge, 2008).

Environmental information and resulting corrosion are collected and analysed through laboratory and field testing (fully described in section 3.4 and 3.5). This data is used to first develop a probabilistic model to estimate CUI rate and depth. Corrosion under insulation is best represented as an isolated discrete non-uniform degradation therefore it is modeled using an extreme value probabilistic approach. The developed model is tested and validated to the experimental data developed through this study. The CUI corrosion rate model is then incorporated into a damage function model for use in fitness for service and risk-based asset integrity evaluations. The damage function model includes many failure modes for an asset under study; the CUI rate model is one important failure mode. This damage function is expanded for use in fitness for service and risk based evaluations. These evaluations include recommended practices and standards such as the American Petroleum Institute's (API) Recommended Practice 581: Risk-Based Inspection Technology ((API RP 581, 2008), Standard, "Fitness-for –Service" (API 579, 2007) and Det Norske Veritas' *(DNV)* Recommended practice, Risk based inspection of offshore topsides static mechanical equipment (DNV RP-G101, 2002). Other more novel approaches (Khan, Haddara, & Bhattacharya, 2006) (Datla, Jyrkama, & Pandey, 2008) are also explored to incorporate the new damage function to improve assessments.

3.4 Design of Experiments for CUI Study

Design of Experiments (DOE) is a systematic strategy to generate information in an efficient manner that captures all the relevant interaction between experimental

factors. This information is acquired such that it contributes to model development in a statistically significant way.

This experimental design follows the three stage design loop detailed in the text as Designing, Planning, and Preparing Corrosion Tests (Roberge, 2003);

1. Statistical design
2. Data Analysis of Results
3. Model development

The statistical design portion of this process is the focus of this paper. Following a statistical design methodology allows for identification of important factors and mechanism of interactions with the smallest number of experimental treatments (Wang & Chang, 2001). This results in a streamlined test regime that minimizes costs and time.

Determination of response variable

DOE is used for all parts of this experimental research. Experiments to determine interactions between factors are first designed using DOE, then the field test and accelerated tests were developed in a similar manner. Experimental data from laboratory and field testing is then used to model CUI rates and develop risk-based

remaining life assessment model for assets under CUI attack. To develop these rates, the corrosion mechanism, initiation time, and rate of corrosion propagation are measured. These are the response variables for all experimental work.

3.4.1 Determination of the effect of environmental factors on CUI using laboratory simulation

Many environmental factors have shown in scholarly work to influence corrosion rate and mechanism. No information was found analysing the combination of these factors. Table 5 lists these important factors that these scholarly work indicate as influencing corrosion rate.

Table 5: Environmental Factors Effecting Corrosion Rate

Environmental Factor	Published Work
Coating	Race, Dawson, Stanley & Kariyawasam, 2007
Temperature	Melchers & Jeffrey, 2008 and DNV RP-G101, 2002
Chloride	Griffin, 2006 and Corvo, Minotas, Delgado & Arroyave (2005)
Microbial	Melchers, 2003, 2008
Time of Wetness	Griffin, 2006 and Corvo, Minotas, Delgado & Arroyave (2005)

The factors listed are used to determine their effect on CUI rate in marine environments and to investigate the interactions between these factors. A factorial design of experiments is used to do this evaluation. Factorial experimental plans help identify the effects of a factor at several levels leading to conclusions that are valid over a range of experimental conditions (Montgomery, 2008).

3.4.1.1 Experimental factor determination

There are four factors under consideration for this experimental plan. These four factors are:

1. Coating
2. Operating Temperature (Internal pipe temperature)
3. Chloride Concentration
4. TOW

Although microbial content was observed by Melchers (2003, 2008) as contributing to corrosion rate, the content of microbial is recorded from the local sea water solution and not considered a controlled experimental factor. This factor elimination is due to the consistency of the local concentration and the use of natural seawater proposed for field testing. This allows further comparison of simulation data to field data.

The levels for each factor are determined from maximum and minimum operational in-situ conditions expected. Factors have at least 2 levels for this work. These levels are listed in Table 6.

Table 6 Factor Levels for Characterization Laboratory Testing

Factor	Level 1	Level 2	Level 3	Level 4
Coating	Coated	Non-Coated		
Operating Temperature	50°C	90°C		
Chloride Concentration	3.2%	3.6%		
Time of Wetness	1 day	7 days	14 days	28 days

Figure 16 illustrates the controllable and uncontrollable factors of the experiment.

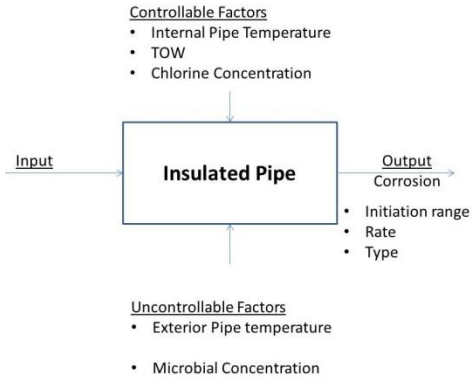

Figure 16 : Experimental Parameters for CUI Characterization Laboratory Test

3.4.1.2 Number of Samples

Design of experiments (DOE) is used to ensure that the effects of all variables are captured along with their interactions using the least number of experimental runs. One method of DOE is factorial design. Using a factorial DOE for three factors at 2 levels yields 8 experimental treatments exposed for 4 different TOW lengths requiring 32 total treatments.

Replication is an important consideration for design of experiments. Replication is used to estimate experimental error and to find a precise estimate of a mean value (Montgomery, Design and Analysis of Experiments (7th Edition), 2008).The cost must be considered against the value of the information gained. Six samples are considered at each treatment level resulting in 192 total samples.

3.4.2 Field Test

The purpose of this field test is to evaluate how corrosion rate and the mechanism of corrosion of LTCS under insulation vary with time under natural environmental conditions at the coast of the North Atlantic.

Field testing is considered an uncontrolled experiment. The environmental conditions cannot be controlled or limited as they occur naturally. Uncontrolled experiments must take into account all possible interaction of the uncontrolled variables or covariates (Baboian, 2005). Covariate values are not affected by experimental factors however they may influence the response and must be included in analysis (Mason, Gunst, & Hess, 2003).

3.4.2.1 Experimental factor determination

The natural environment and exposure time are the factors that need to be considered in the field test. The time of exposure is the only parameter that can be controlled. The temperature of the internal pipe is controlled and held steady. Environmental conditions are uncontrollable and are considered covariant for this work.

To evaluate CUI in field conditions, the following uncontrolled variables are measured:

- External pipe temperature
- Amount of Precipitation

- Chloride content of precipitation
- Time of wetness (TOW)
    - Atmospheric temperature
    - Relative Humidity

The controlled variables in this field test are:

- Internal pipe temperature
- Time of exposure
- Coating

The responses (dependant variables) in this field test are corrosion rate and corrosion mechanism. Figure 17 illustrates the experimental parameters of the field test. This field test measures and records both controllable and uncontrollable factors along with the corrosion response.

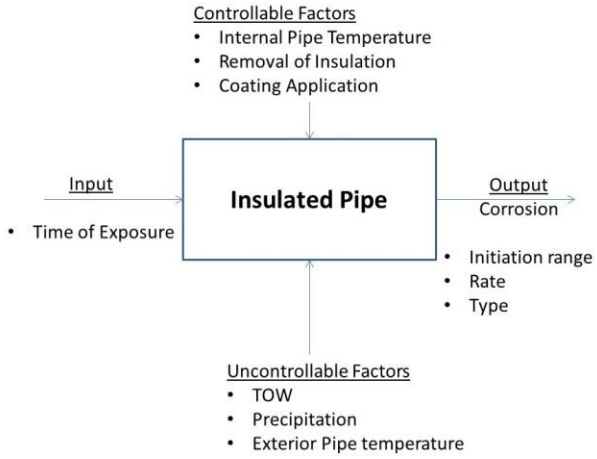

Figure 17: Experimental Parameters for Field Test

3.4.2.2 Number of Samples

For this field test, the principle purpose is to determine how corrosion rates vary under insulation in a natural environment. The American Society for Testing Materials (ASTM) standard ASTM G50 (2010) "Standard Practice for Conducting Atmospheric Corrosion Tests on Metals" is used as a guide to determine the number of samples (ASTM G50, 2010). This experiment requires removal of insulation, visual inspection, and possibly removal of a sample from the test site at periodic times throughout the field test. Based on field testing of CUI in work done by Williams and Evans (2010) that indicates a 4 month inspection period and ASTM G50 that suggests a yearly inspection period, an interval of 6 months has been chosen for this experiment (Williams & Evans, 2010) (ASTM G50, 2010). To ensure reliable results, three specimens are available for inspection at each time interval.

To gather long term data, a three year field test experiment is planned. Forty-two insulated samples are exposed at the beginning of the test with 12 un-insulated control samples for a total of fifty-four samples. Half of all samples are protected with an industry approved coating. Six insulated samples and two un-insulated control sample are inspected at each of the 6 intervals. The inspected specimens are returned to the test if possible to gather information on the effect of re-insulation on corrosion rates.

3.4.3 Accelerated Marine Atmosphere Testing for CUI

The development of a more accurate accelerated CUI test is needed to determine CUI rates for different applications. This allows for rate determination of different test couples (insulation and pipe material), alternative coatings, and different environmental conditions without the long term commitment of expensive field tests.

3.4.4 Experimental factor determination

The accelerated CUI test uses data collected during the field test in the natural setting to accelerate CUI in the laboratory. Conditions are controlled to simulate the natural environment found in the first year of field testing (one cycle). This natural cycle is accelerated and repeated to simulate longer exposure time.

This repetition of the environmental cycle is the factor under consideration for this experiment. Ten levels of this factor are used to simulate five years of exposure. The first six levels correspond to the inspection intervals of field testing and the remaining 4 levels indicating an additional 2 years of exposure. Figure 18 shows the experimental parameters for the acceleration test.

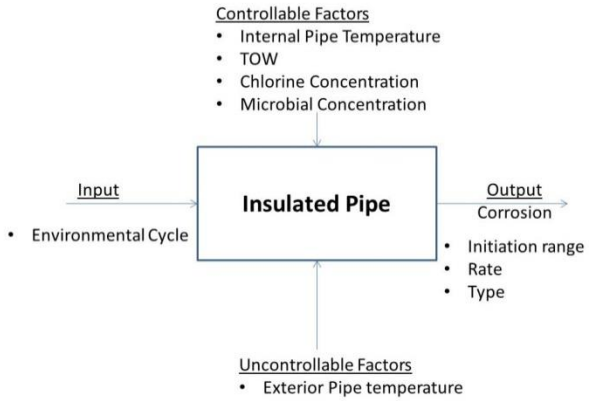

Figure 18: Experimental Parameters for Accelerated CUI Testing

3.4.4.1 Number of Samples

The standard test set up in ASTM G189, Standard Guide for Laboratory Simulation of Corrosion Under Insulation (ASTM G189, 2007) allows for two sets of three specimens to be evaluated for each experimental treatment. Table 7 illustrates each treatment.

Table 7: Laboratory Simulation Design of Experiments Part 1, Accelerated Marine atmosphere testing

Factor Level	Description	Simulated time (Years)	Number of Samples
1	First half of environmental cycle conditions	0.5	6
2	1.0 cycle of environmental conditions	1.0	6
3	1.5 cycles of environmental conditions	1.5	6
4	2.0 cycles of environmental conditions	2.0	6
5	2.5 cycles of environmental conditions	2.5	6
6	3.0 cycles of environmental conditions	3.0	6
7	3.5 cycles of environmental conditions	3.5	6
8	4.0 cycles of environmental conditions	4.0	6
9	4.5 cycles of environmental conditions	4.5	6
10	5.0 cycles of environmental conditions	5	6

A total of 60 samples are used in part 1 of the laboratory simulation and acceleration experiments. The factor levels are applied in random order to reduce possible bias.

3.4.5 Interaction

Understanding the interaction between different factors is important to developing a predictive model of CUI rate. These experimental plans investigate these interactions. Individually, the Table 8 indicates the expected reaction of corrosion rate (CR) or corrosion mechanism of the four controlled factors.

Table 8: Expected reaction of experimental factors on corrosion rate and corrosion mechanism

Factor	Expected Reaction
Coating	Decrease in general corrosion, possible increase in localized corrosion
Operating Temperature	Increase CR with increased temperature
Chloride Concentration	Increase CR with increased concentration
Time of Wetness	Increase CR with increased TOW

3.5 Experimental Design

To conduct the experimental plans developed in section 3.4.4, experimental designs of each test plan were developed. These designs are developed from well recognised standard practices and are adapted where possible to satisfy the unique demands of each.

3.5.1 Laboratory Testing

The laboratory tests are based on ASTM G189-07 Standard Guide for Laboratory Simulation of Corrosion Under Insulation (ASTM G189, 2007). This simulation allows for many critical factors for CUI simulation including:

- Control of annular space between pipe and insulation
- Internal heating to produce hot pipe surfaces
- Controlled introduction of electrolyte

A representative schematic of the ASTM G189-07 test setup is included in Figure 19 and Figure 20.

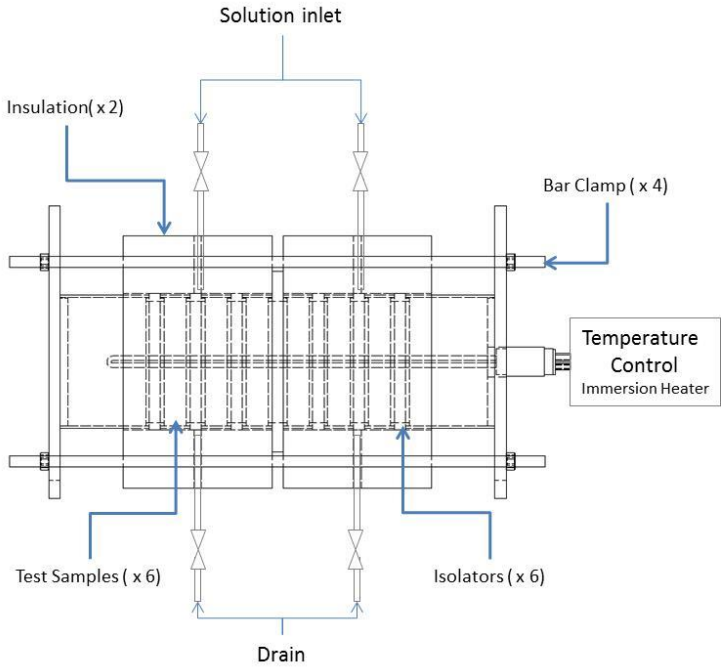

Figure 19: Schematic of CUI simulation Cell (ASTM G189, 2007)

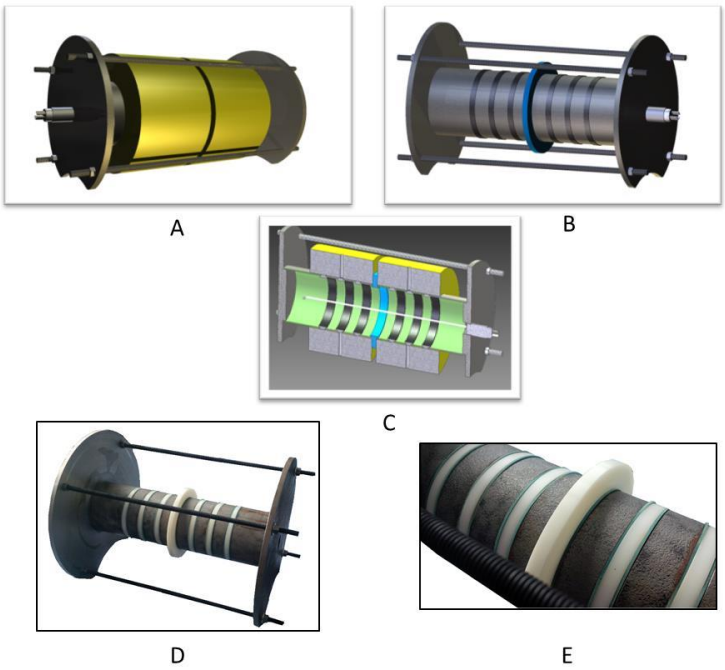

Figure 20: CUI Laboratory test cell. A: Model of complete cell including insulation. B: Model of cell with insulation removed. C. Model of cross section of full cell. D: Cell without insulation. E: Cell without insulation showing spacers, samples, and dam. (ASTM G189, 2007)

The laboratory tests are based on ASTM G189-07 “Standard Guide for Laboratory Simulation of Corrosion Under Insulation” (ASTM G189, 2007). The test procedure in the standard is adapted to simulate the conditions of the field test. The same pipe, insulation, coating, and solution observed in field testing are evaluated in the laboratory simulation. Kane & Chauviere (2008) also adapted this standard to evaluate thermal spray aluminum coating on steel under insulation and determine corrosion rates under different insulation types (Kane & Chauviere, 2008).

One important variation from the standard is the electrochemical measurement technique. ASTM G189-07 specifies is Potentiodynamic Polarization Resistance (PPR) to determine corrosion rates. While this method is useful for determining corrosion rates is in laboratory testing, PPR calls for the inducement of controlled potential and is thus limited in determining the naturally occurring corrosion expected in field testing where the inducement would alter the measured current. To combat this issue, electrochemical noise (EN) techniques are used in both lab and field testing. EN is a passive method of corrosion monitoring where no applied current or potential is required (Frankel, 2008). This method records deviation from the naturally occurring electrochemical potential and current (Reiner & Bavarian, 2007; Huet, 2006) indicating when corrosion occurs. Pitting and other forms of localised corrosion have been detected using this method with good correlation (Estupiñán-Lópezst al. 2011). Eden and Kane (2005) applied this method using a single electrode monitoring probe where the structure was used as a current return path. This is a novel application and there are challenges to

overcome to adapt the technology to this application. External noise can interfere with EN measurements including (Huet, 2006):

- Vibrations
- electromagnetic
- Surface changes
- Electrolyte velocity

Determining wetted surface area and ensuring surface coverage are additional issues for investigation. This technique will help determine corrosion rate and mechanism however, the main purpose is to investigate EN as a technique to indicate corrosion activity for in-situ monitoring as a means to improve inspection scheduling.

3.5.1.1 Characterization Laboratory Testing

Characterization tests are run to determine the effects of key variables on corrosion rate and mechanism. The effects of coating, operating temperature, chloride concentration, and time of wetness are assessed and possible interactions analysed.

3.5.1.2 Accelerated laboratory testing

Accelerated laboratory tests are conducted after accumulation of one year of data from field testing.

Acceleration is accomplished by reducing the yearly cycle by removing the time elapsed where no corrosion is indicated in the field test. This time is determined from a proposed online electrochemical monitoring system and TOW data collected during the first year of field testing. Cyclic wetting and drying of the pipe surface is expected with no corrosion expected during the dry periods. This dry period is minimized, allowing for accelerated simulation of the field test.

From the field test the following factors are determined and controlled in the laboratory:

- Pattern of TOW at pipe surface
- Chloride concentration
- Temperature difference

The test is run to simulate 3 years of service and validated with subsequent years of field test data.

3.5.1.3 Field Testing

In field tests, environmental conditions and electrochemical noise measurements are recorded and analyzed to understand how corrosion rates and types of

corrosion are affected by the environment. The test location is at the shoreline in Argentia, Newfoundland and runs for 3 years to collect and analyze CUI in a marine setting under different environmental loading. Figure 21 shows the location of the test site. Argentia, NL was chosen to most closely replicate conditions offshore. As the location is on a small peninsula in a large bay, it is reasonable to consider the majority of prevailing winds to simulate offshore conditions.

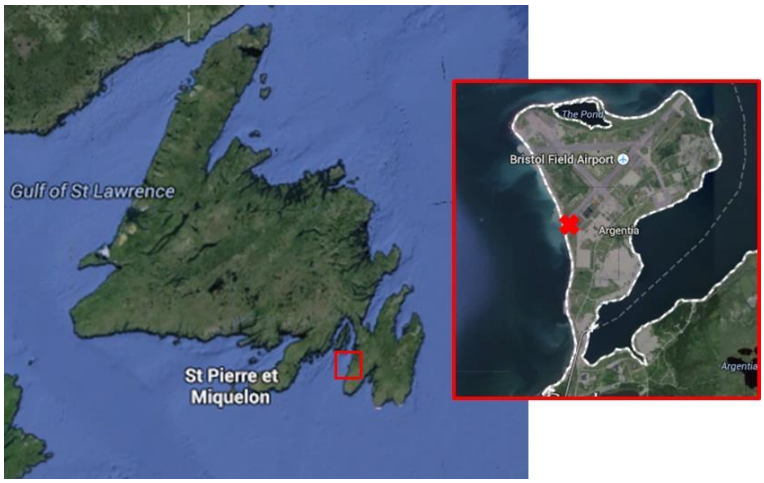

Figure 21: Field test location. Island of Newfoundland, Argentia location (Google, n.d)

The goal of this Field test is to understand what effect time, temperature, chloride content, time of wetness (TOW), internal and external temperature and possible re-insulation have on the corrosion behaviour of LTCS under insulation. There is no standard field test procedure to study CUI in field conditions. To measure and control these factors; an experimental test fixture is designed to satisfy the following requirements:

- Fifty two test cells, available for periodic removal from test sight
- Internal pipe temperature >60 °C (operating temperatures up to 90°C with outliers above 100°C)

Design of this field test is based on the requirements determined through the DOE, ASTM standards for field testing and CUI assessment, and a field test conducted in an industrial environment to compare the effects of insulation type on CUI.

A study (Williams & Evans, 2010) conducted in Northborough, MA used an outdoor test fixture to evaluate CUI. Figure 22 illustrates the field test set-up used. This study was conducted in an industrial environment to determine changes in corrosion under different types of insulation.

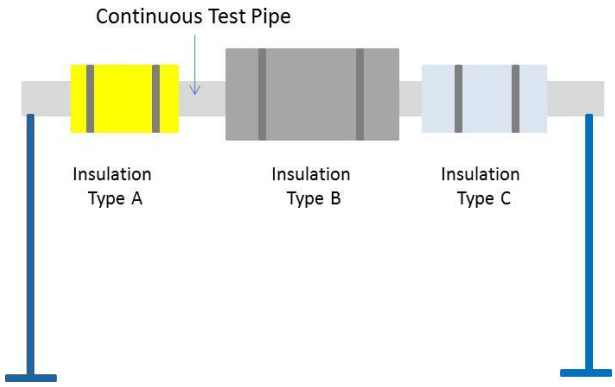

Figure 22: Sketch of Industrial test set up (Williams & Evans, 2010)

The test fixture for the CUI field test is similar in design. The supporting structure is constructed from pressure treated lumber to ensure no interaction with test samples.

An initial design of the experimental set-up is shown in Figure 23.

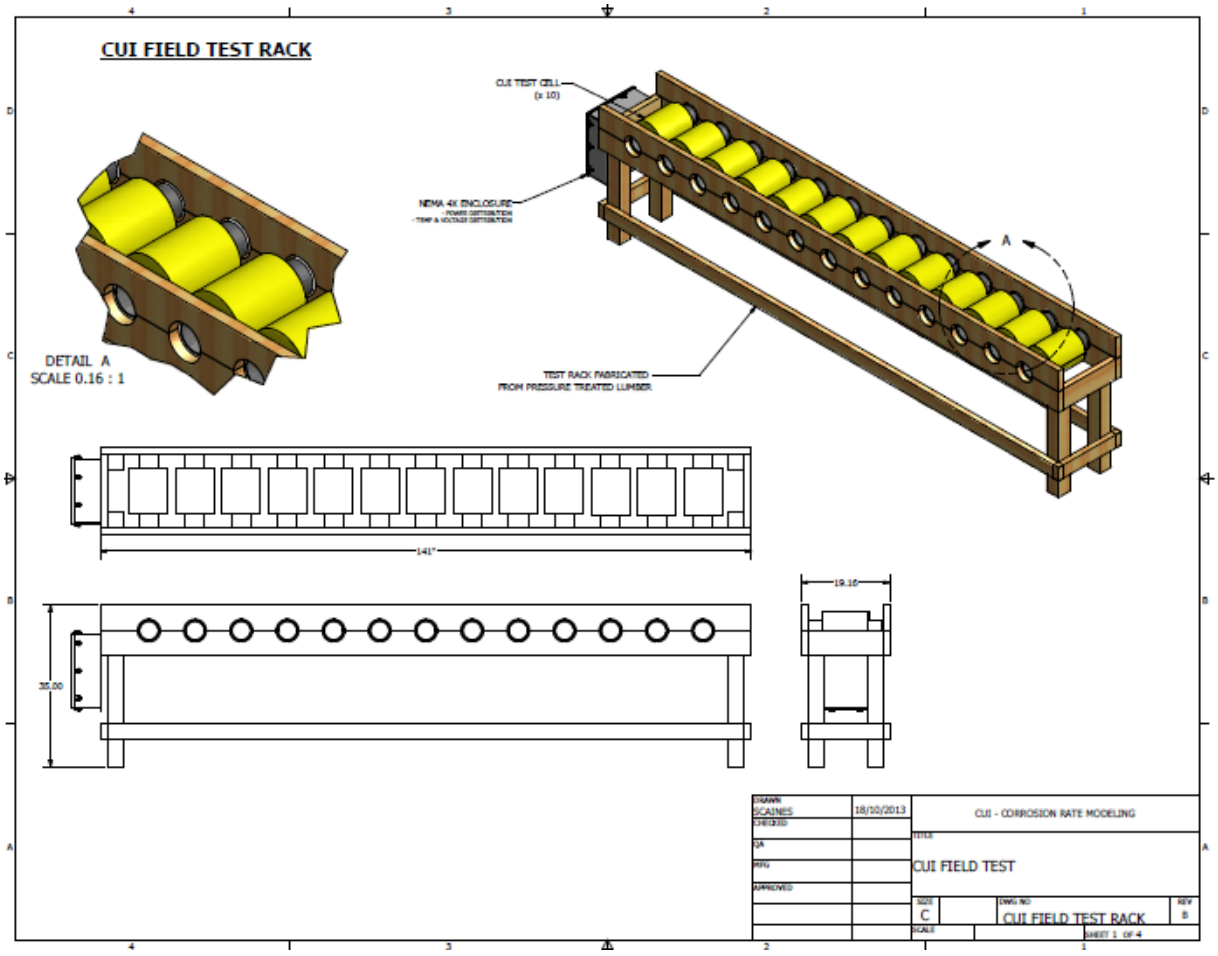

Figure 23: Proposed Field Test Fixture

Each test rack includes thirteen test cells. To accommodate the required fifty two samples, four test fixtures are needed. Each test cell is created in the same manner with the same materials, creating base homogeneous experimental unit for experimentation. The test cell is shown in the drawing below (Figure 24).

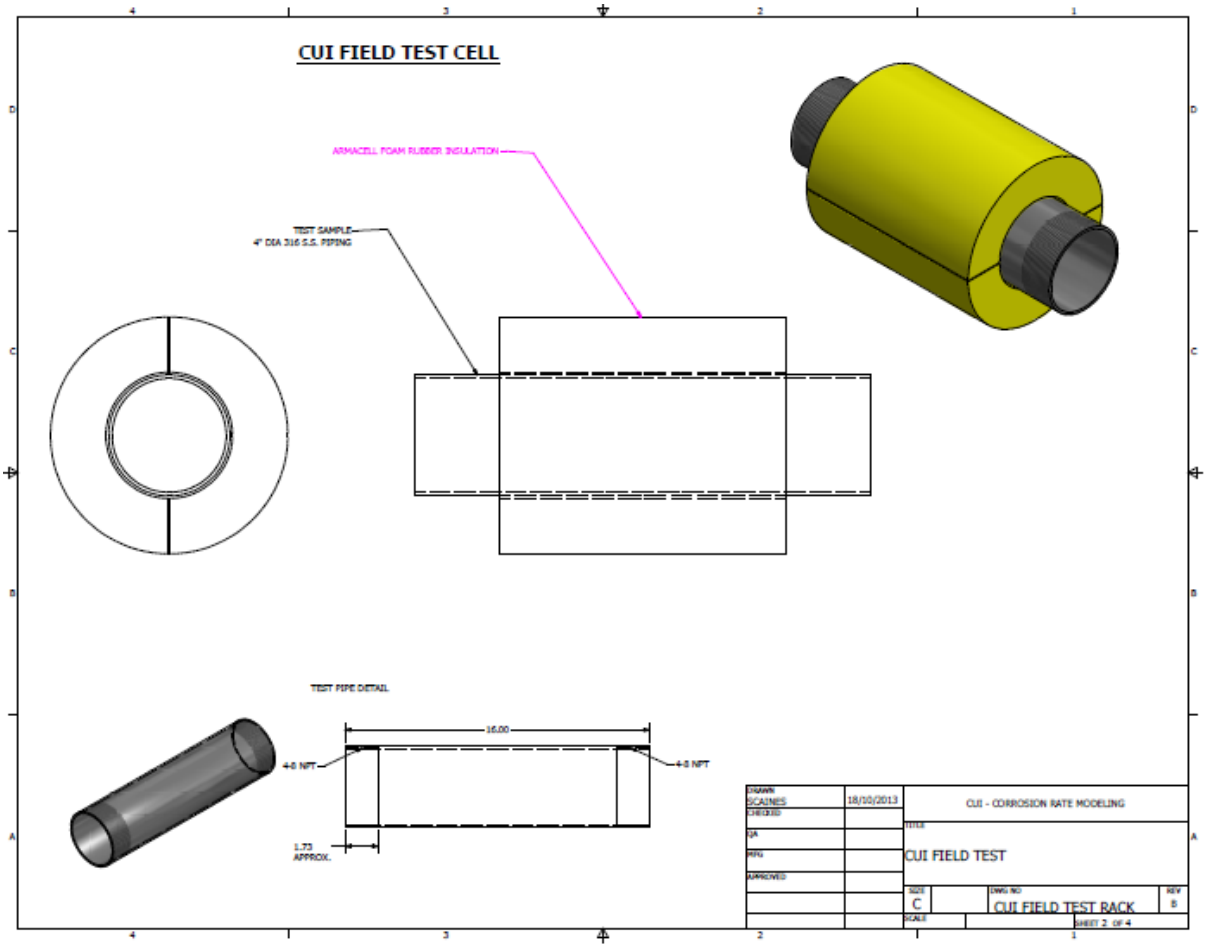

Figure 24: Field Test Cell

Each cell is a self-contained experimental unit and includes:

- LTCS Pipe section
    - 16 in. total length
    - 4” nominal diameter
    - National Pipe Thread (NPT) threads

- Thermal insulation
    - Two piece system with silicone at seam
- Oil immersion heater
    - 500W
- Thermocouple for heater control

3.5.2 Data Acquisition

Different measurement techniques are used to evaluate corrosion rate and mechanism. Controlled and uncontrolled variables are also measured and recorded.

3.5.2.1 Controlled and Uncontrolled Variables

These experiments require many data acquisition techniques to capture the variable conditions of the controlled and uncontrolled variables needed to understand and predict CUI. These measurements are summarised below in Table 9.

Table 9: Summary of Variable Data Acquisition

Variable	Description	Lab	Field	Note
Internal pipe temperature	Measured and controlled using an immersion thermocouple	√	√	Controlled and recorded for all experiments
External pipe temperature	Measured with a thermocouple mounted between the pipe and insulation on each test cell	√	√	Measured and recorded for all experiments
Atmospheric temperature	Monitored using a Portable Temperature Relative Humidity Data Logger	√	X	Measured and recorded for all Field experiments
Atmospheric TOW	Monitored using a Portable Temperature Relative Humidity Data Logger placed at the test site	√	X	Measured and recorded for all Field experiments
Test Cell TOW	Measured at the pipe surface using methods adapted from ASTM Standard G84 – 89 "Standard Practice for Measurement of Time-of-Wetness on Surfaces Exposed to Wetting Conditions as in Atmospheric Corrosion Testing"	√	√	Measured at the pipe surface using methods adapted from ASTM Standard G84 – 89 "Standard Practice for Measurement of Time-of-Wetness on Surfaces Exposed to Wetting Conditions as in Atmospheric Corrosion Testing"
Chloride content	Collected using local area data collected by third party and local site sampling.	√	√	ASTM G140 "Standard Test Method for Determining Atmospheric Chloride Deposition Rate by Wet Candle Method" can be used to indicate deposition of Cl and to classify severity of the environment
Microbial Content	Microbial Content	√	√	Measured and recorded for all experiments
Precipitation amount	Manually collected and compared with local published data	√	X	Measured and recorded for all Field experiments
Electrochemical Noise	Measured using a three identical electrode methodology	√	√	Measurement technique based on ASTM G199-09 "Standard Guide for Electrochemical Noise Measurement" and "An alternative to the use of a zero resistance ammeter for electrochemical noise measurement: Theoretical analysis, experimental validation and evaluation of electrode asymmetry" by Curioni, Balaskas & Thompson (2013)

A schematic of the data acquisition plan is included in Figure 25 below.

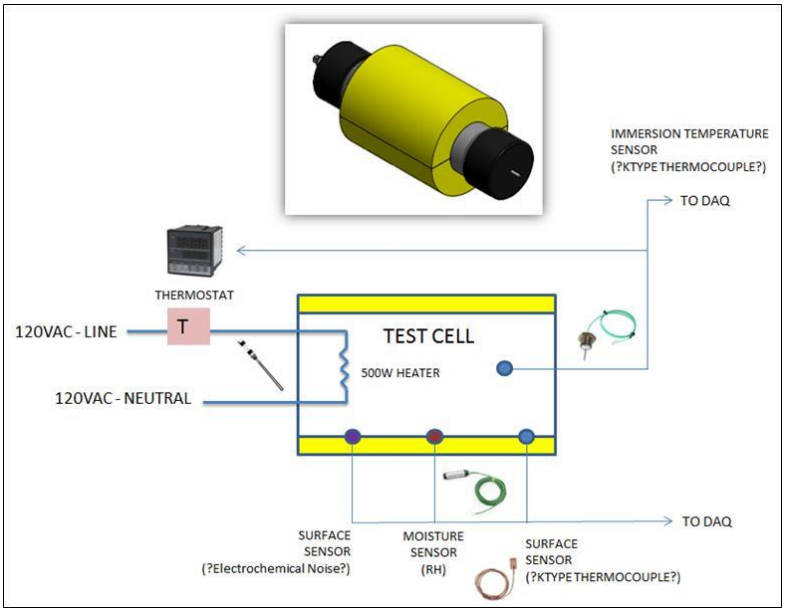

Figure 25: Field test data acquisition preliminary block diagram

3.5.2.2 Response Variables

Corrosion rate and mechanism are evaluated and quantified for each experiment using inspection and electrochemical measurements. Inspections are conducted after each experimental run for laboratory testing and at each 6 month interval for field testing. These inspections include visual inspection, mass loss evaluations, and non-destructive evaluations including liquid penetrant inspection (LPI). Further evaluation will be performed if required to confirm rate and mechanism using destructive evaluations including optical microscope and scanning electron microscope (SEM). Electrochemical noise (EN) measurements are continuously recorded to determine corrosion ranges, corrosion rate, and corrosion mechanism.

Inspection and EN information is compared to determine rates and mechanism of CUI.

Field test samples that require destructive evaluations are not returned to the test site. Figure 26Figure illustrates the field test cycle.

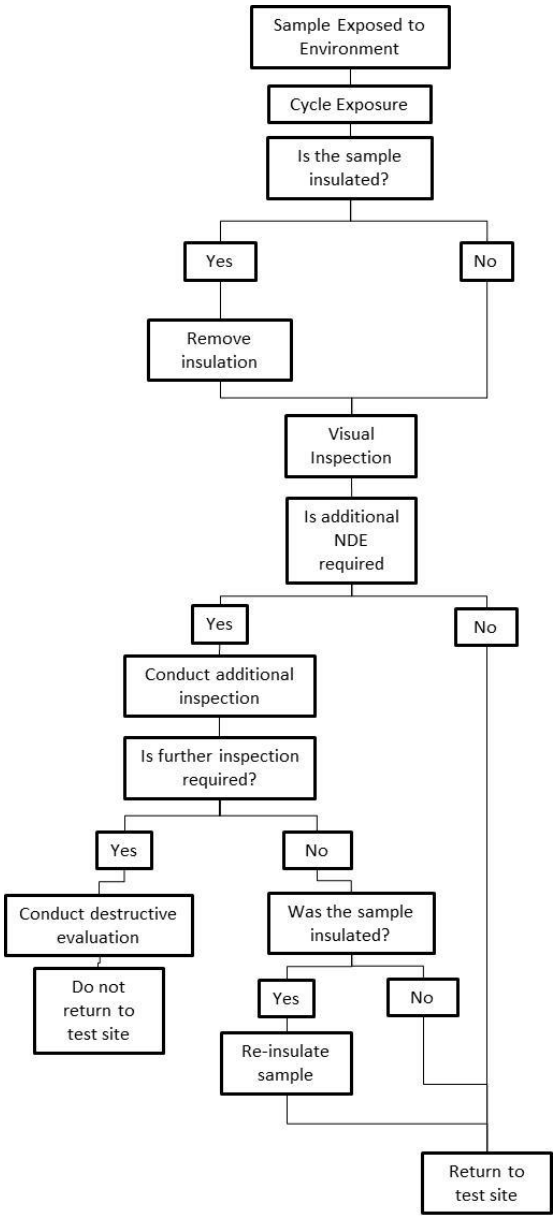

Figure 26: Inspection Cycle

3.6 Data Analysis

3.6.1 Laboratory testing

Data collected in both laboratory experiments is analysed to determine the effect on corrosion rate and mechanism. Direct and indirect relationships are explored and factor integration graphs used to identify and interpret interactions (Montgomery, 2008).

3.6.2 Field testing

As discussed in section 3.4.2, the nature of field testing is difficult to analyse. The uncontrolled variables (covariates) have the potential to dramatically affect the rate and mechanism of corrosion. A covariate is an uncontrollable variable that can affect the response but is not affected by the controlled experimental factors. The effects of these variables are found through analysis of covariance (ANCOVA) (Montgomery, 2008; Mason et al., 2003). This procedure is used to understand the effect of environmental conditions on corrosion in field testing.

For the field test, there are three controlled factors and five covariates. General regression techniques are used to determine the significance of all factors and to develop a model to predict corrosion rate (Hicks & Turner, 1999). Table 10 below illustrates the input that is used to determine a mathematical model.

Table 10: Field Test Analysis

Field Test	Controlled			Covariate					Response
Observation Number	Time (months)	C	I	T (x_{1j})	P (x_{2j})	[CL] (x_{3j})	TOW (x_{4j})	MC (x_{4j})	**CR (y_{1j})**
1	6	1	1	x_{11}	x_{21}	x_{31}	x_{41}	x_{51}	Y_{11}
2	6	1	1	x_{12}	x_{22}	x_{32}	x_{42}	x_{52}	Y_{12}
3	6	1	1	x_{13}	x_{23}	x_{33}	x_{43}	x_{53}	Y_{13}
4	6	0	1	x_{14}	x_{24}	x_{34}	x_{44}	x_{54}	Y_{14}
5	6	0	1	x_{15}	x_{25}	x_{35}	x_{45}	x_{55}	Y_{15}
6	6	0	1	x_{16}	x_{26}	x_{36}	x_{46}	x_{56}	Y_{16}
7	6	1	0	x_{17}	x_{27}	x_{37}	x_{47}	x_{57}	Y_{17}
8	6	0	0	x_{18}	x_{28}	x_{38}	x_{48}	x_{58}	Y_{18}
n	36	C	I	x_{1n}	x_{2n}	x_{3n}	x_{4n}	x_{5n}	Y_{1n}

C= Coating, I = insulation, 1= yes, 0 = No, T = Temperature, P = Precipitation, TOW= time of wetness, MC = Microbial content, CR = Corrosion rate

Due to the length of study and unexpected effects of the harsh test site conditions on sensor equipment, the collection and analysis of this data is not included in this thesis.

3.7 Future work

The relationships discovered and data collected will be analyzed to develop a predictive model for corrosion rates under insulation. Experimental data from laboratory and field tests will first develop a probabilistic model to estimate CUI defect rate and defect depth. Corrosion under insulation is best represented as an isolated discrete non-uniform degradation therefore; it is modeled using an extreme value probabilistic approach. The developed model will be tested and validated against the experimental data developed through this study. The CUI corrosion rate model will then be incorporated into a damage function to be used

in fitness for service and risk-based asset integrity evaluations. The damage function will include many failure modes for an asset under study; the CUI rate model is one important failure mode. This damage function will then be expanded for use in fitness for service and risk based evaluations. These evaluations include recommended practices and standards such as API Recommended Practice 581: Risk-Based Inspection Technology ((API RP 581, 2008), API standard, “Fitness-for–Service” (API 579, 2007) and *DNVs Recommended practice, Risk based inspection of offshore topsides static mechanical equipment* (DNV RP-G101, 2002). Other more novel approaches (Khan, Haddara, & Bhattacharya, 2006) (Datla, Jyrkama, & Pandey, 2008) will be explored to incorporate the new damage function to improve assessments. The validated model and improved method will be unique to the condition observe in the region. It will serve as an important tool to assess fitness for service, estimate remaining life, plan inspection and maintenance intervals**.**

3.8 **Conclusions**

This paper illustrates that careful evaluation of field and laboratory experimental data makes a significant contribution towards understanding and preventing the detrimental effects of CUI in the offshore industry. This work:

- Develops a field test procedure to study corrosion under insulation (CUI) in marine environments that ensures that data collected is representative of CUI developed in the offshore industry. The field test site is designed to

capture CUI development as seen in industry. The site is flexible in design to accommodate future study of CUI issues in the industry.

- Determines a method to capture the mechanism and rate of CUI development in harsh marine environments to further understand CUI and aid in damage prediction.

- Creates a method to evaluate electrochemical noise measurement as a tool for on-line corrosion monitoring. The ability to economically monitor piping systems for CUI can further reduce risk and increase safety.

- Develops a program to simulate and accelerate CUI in a laboratory to realistically predict long term service life by understanding CUI in a natural setting. From long term testing in marine environment, an environmental cycle that can be accelerated in a laboratory test is determined. This cycle can be used to simulate long term corrosion rates for other material/insulation configurations and to further understand CUI mechanisms.

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4.0 Simplified Electrochemical Potential Noise method to Predict Corrosion and Corrosion Rate

Preface

A version of this paper was submitted for publication to the Journal of Loss Prevention in the Process Industries. Peer feedback was received; paper is revised and resubmitted, awaiting final decision (as of October 2016). Susan Caines is the primary author for this work. Co-authors for this manuscript include Dr. Faisal Khan, Dr. John Shirokoff, and Dr. Dr. Yahui Zhang. The primary author developed the conceptual model, the design of experiments, experimental design, completed experiments, results and analysis and prepared the first draft of the manuscript. The co-author Faisal helped in developing the concept, experimental setup and testing of the concepts, reviewed and corrected the models and results, and contributed in preparing, reviewing and revising the manuscript. The co-author Dr. Yahui Zhang contributed through support in the development and improvement of the design and assisted in concept analysis development and assisted in reviewing and revising the manuscript. The co-author Dr. John Shirokoff contributed through support in the development and improvement of the design and assisted in reviewing and revising the manuscript.

Abstract

Corrosion is a costly and dangerous issue in most industries causing breakdown of equipment, increased downtime and potential risk to personnel. Corrosion under

insulation (CUI) is a significant contributor to these issues. As CUI is difficult to detect, real time monitoring is an important part of identifying, controlling and preventing this serious issue. Electrochemical noise (EN) is a promising technique that can be applied to components under insulation. Issues with traditional EN techniques when applied to field conditions necessitate the need for simplified methods to incorporate the benefits of EN monitoring to in-situ application. By using three identical electrodes made of the same materials as the bulk materials in production to simulate the corrosion behavior, this research introduces a simplified methodology using measured electrochemical potential noise (EPN) to predict the corrosion rate of individual electrodes and demonstrates its application through short term testing. A relationship between isolated electrode EPN, mass loss and corrosion rate was found for electrodes undergoing corrosion. The relatively high impact of retained corrosion product in short term tests for electrodes undergoing localized corrosion was found to contribute to the reduced correlation in the EPN-mass loss relationship. The relationship between EPN and corrosion rate was found to be dependent on immersion times with longer immersion times demonstrating higher correlation than shorter immersion time tests.

Keywords: Corrosion, electrochemical potential, online monitoring, electrochemical noise, corrosion under insulation

4.1 Introduction

Corrosion is a significant issue in industries around the world with an estimated $170 billion spent throughout all industries in the United States (Adesanya A.O., Nwaokocha C.N., & Akinyemi O.O., 2012). The recent NACE IMPACT study (2016) updates the global cost of corrosion to US$ 2.5 trillion. This cost is significant and is of particular interest to operators in the Oil and Gas Industry. The impact of corrosion on the oil and gas industry was estimated by Kermani and Harrop (1996) as 25% of all failures. These failures have a direct impact on safety, production and profit. One significant cost due to corrosion is due to repairs and replacements. Improvement of maintenance planning and inspection procedures is one way to begin reducing costs and improving safe operations throughout the industry. Within the offshore oil and gas industry one significant issue is corrosion under insulation (CUI).

CUI is a widespread issue in industrial operations. Offshore oil and gas production facilities routinely use insulation to regulate process temperatures and protect personnel. If corrosion occurs under insulation, limited visual access can permit this degradation to continue unchecked until discovered through inspection and maintenance programs or by component failure.

Insulation is designed to limit, reduce, and in some cases eliminate moisture penetration to the pipe surface however; CUI remains an issue as there are still opportunities for moisture to penetrate insulation barriers and create corrosion conditions. Maintenance and use, improper installation, wear and tear, difficult

geometries and extreme conditions are a few possible causes of corrosion condition development under insulation. As operations move further into extreme environments, the use of insulation will likely increase and the probability of CUI will also increases.

As CUI is difficult to detect (Caines, Khan, & Shirokoff, 2013) and is the primary cause of pipeline failures (Nicola, Carreto, Mentzer, & Mannan, 2013). Continuing work is needed to improve both inspection techniques and planning and real-time monitoring. An integrated sensor network using two impedance measurements strategies and a modified Radio-frequency identification (RFID) tag strategy was examined by Ayello, Hill, Marion, and Sridhar (Ayello, Hill, Marion, & Sridhar, 2011). They found that while impedance can be used to detect CUI, it may require significant investment in the number of sensors. They also noted that RFID tag sensors are potential solutions however there were issues with data recording. One recent work by Funahashi (2014) describes a "CUI warning system" to indicate when corrosion conditions are present. This system uses titanium and aluminum wires in fiberglass tape that produce a potential difference when moisture is present indicating corrosion conditions. This method uses potential difference to detect corrosion conditions while other techniques use similar principles to detect and determine corrosion and its rate. Other techniques that use electrochemical phenomenon to monitor and quantify corrosion are techniques like electrical resistance (ER), Linear Polarization resistance (LPR) and Electrochemical noise (EN). These techniques use the inherent properties of

corrosion to qualify and quantify corrosion behaviour. Birketveit & Stipanicev (2016) identified these methods for monitoring corrosion in side-stream units however their review of case studies did not identify any studies using EN as a monitoring technique.

Ongoing work by the authors includes a comprehensive research plan to investigate CUI through laboratory and field testing. The work aims to understand the rates and mechanisms of CUI develop monitoring techniques leading to improved prediction and risk assessment techniques (Caines, Khan, Shirokoff, & Qiu, 2015). This work identified Electrochemical Noise (EN) as a promising tool for field evaluations of CUI. During this study, initial research and laboratory testing highlighted the difficulty in using EN measurements in the field. This is partially due to the high number of samples and length of testing required as well as the difficulty in controlling environmental noise that can affect the measurements. To combat these issues, a simplified EN method was developed that uses Electrochemical Potential Noise (EPN) measurement data to indicate when corrosion may be occurring and to predict a likely rate of mass loss for the system. This method is demonstrated using three identical electrodes made of the same materials as the bulk materials in production to simulate corrosion behavior. This work is a continuation of research by the authors and is the next step in validating the simplified EN method for ongoing CUI field work.

4.1.1 Electrochemical noise (EN)

Electrochemical noise (EN) is a passive technique used primarily in laboratory work to evaluate corrosion rates and identify corrosion mechanism. EN was first discussed by Iverson (1968) and has been explored and developed since that time. When corrosion occurs, measurable changes in free corrosion current and potential can be measured. This technique evaluates naturally occurring corrosion without external inputs that could affect the results.

EN is evaluated by analysing either (or both) voltage and current noise on a corroding system. EN methods have been widely researched and developed for corrosion evaluation and study. Electrochemical noise methodologies such as those outlined in ASTM G199 (ASTM G1, 2003 (2011)) and in the works of Bihade, Patil, & Khobragade (2013), Cottis (2001), and Girija et al (2005) . These works and many others (Bertocci, Huet, & Nogueira, 2003; Brusamarello, Lago, & Franco, 2000; R. Cottis, 2006; De Cristofaro, Luperi, Miceli, Conde, & Williams, 2001; Naing, Wong, & Tan, 2006) illustrate how EN can be a useful tool in determining corrosion rates and in determining corrosion mechanism such as pitting. Naing, Wong, & Tan (2006) developed a new technique to evaluate CUI that applies EN to determine moisture penetration under insulation using wire beam electrode (WBE) methods. These methods measure potential change against a SCE reference electrode. They determined that a WBE sensor could be used to monitor moisture penetration through different types of simulated insulation using noise signature analysis.

4.1.1.1 Traditional EN techniques

Traditional EN techniques measure both the potential and current of a corroding system and records the naturally occurring changes (noise) to determine both corrosion rates and corrosion mechanisms. A traditional set-up for electrochemical noise is a three electrode system including a working (WE), auxiliary (or counter) (AE) and reference (RE) electrode. Current (A) between the WE and AE is usually measured through a zero resistance ammeter (ZRA) and the potential (V) is measured between the WE and AE pair and the RE through a voltmeter as illustrated in Figure 27.

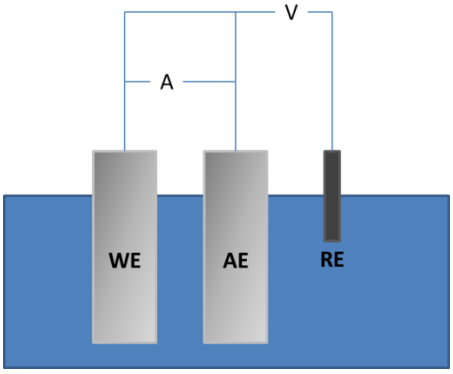


Figure 27: Schematic of a typical EN measurement set-up

The WE is the corroding metal and the AE can be a low reaction metal or an electrode nominally identical to the WE. The RE can be a standard reference electrode or a third nominally identical electrode.

The use of standard reference electrodes in field applications is difficult and a three identical electrode system is more practical for field experiments and in-situ

monitoring (Bertocci et al., 2003). This type of three identical electrode set-up is the focus of this work.

4.1.1.2 Three identical electrode EN technique

In a three identical electrode EN measurement system as shown in Figure 28, all electrodes (working, auxiliary and reference) are nominally identical. Unlike with the use of a noiseless RE, the third identical reference electrode generates noise. For general corrosion it is more likely that the noise generated by all electrodes is similar. By wiring three identical electrodes together, this system may simulate the actual corrosion behaviour of large bulk items used in practice, which are made of the same material as the electrodes.

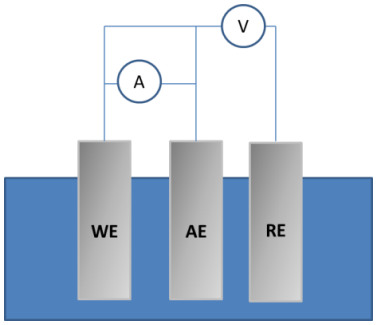


Figure 28: Schematic of a three identical electrode system

4.1.1.3 Issues with Current EN Techniques

Both of the methods shown in Figure 27 and Figure 28 are difficult to apply in field conditions with the measurement of corrosion current being especially difficult. Current measurements for corrosion are very small, in the range of picoamp to microamp. This measurement can be affected by non-corrosion related noises

that overshadow the corrosion current. These non-corrosion noises are magnified in the field and are impossible to control or eliminate. To combat this, specialized equipment is needed (Zero resistance ammeter or picoammeter). The issue with this type of equipment is that it is generally expensive and can be used for only one channel of measurement. This equipment is excellent for laboratory evaluation however does not lend itself to field application where multiple systems need to be monitored and the cost and complexity would be unreasonably high.

4.1.2 Analysis of Electrochemical Noise Measurements

Electrochemical Current Noise (ECN) and Electrochemical Potential Noise (EPN) time records are analysed in varying degrees of complexity to determine information about corrosion behaviour.

When a metal corrodes, there are measureable changes in the potential and current due to the corrosion. These changes (noise) can be interpreted to determine corrosion mechanisms and corrosion rates (Eden, Meng, Mendez, & Yunovich, 2011).

Corrosion information can be found most simply by examination of the time record (current or potential) to look for trends and qualitatively determine corrosion mechanism (general, pitting) and to estimate corrosion rates, (ASTM G1, 2003 (2011)).

4.1.2.1 Corrosion Mechanism Determination

Changes in the geometry of both EPN and ECN time records can indicate the type of corrosion occurring. The illustration in Figure 29 demonstrates how these differences in the time record can be interpreted as an indication of corrosion mechanism.

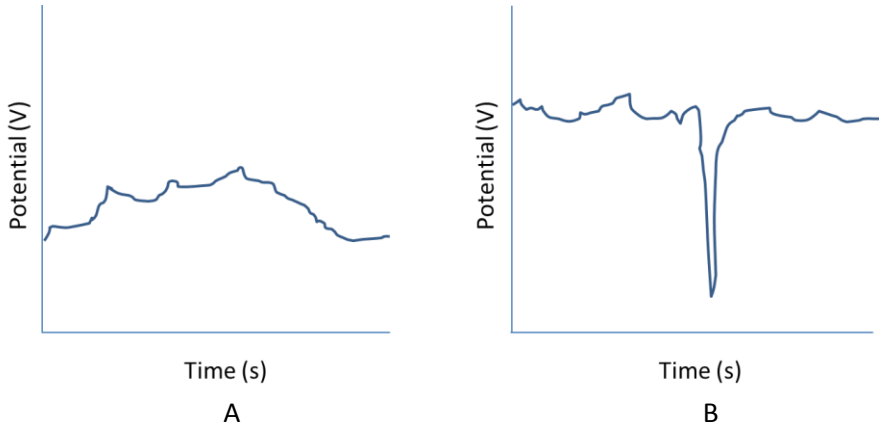


Figure 29: Illustration of time records indicating possible corrosion mechanism. Representative images are not based on collected data. A. General corrosion. B. Localized corrosion

This type of analysis is used along with other more complex methods to aid in determining corrosion type (Al-Mazeedi & Cottis, 2004; Eden et al., 2011; Girija et al., 2005; Rios, Zimer, Pereira, & Mascaro, 2014).

Jian et al (2013) use typical features from EN time records as training for neural networks to assist in corrosion mechanism type identification. They indicate peaks as seen in Figure 29B are indicative of pitting and irregular oscillation as an indication of general corrosion.

Beyond examination of the EN time records, Cottis (2006) indicates that impedance spectrum analysis may be able to provide information on corrosion type with continued study. This work also indicates that there is a need for a simplified method to determine information about corrosion from unprocessed data.

4.1.2.2 Corrosion Rate Determination

Current techniques and methodologies aim to interpret EN data to determine a corrosion rate. These methods generally employ complex filters and data analysis methods. Table 11 lists a few sources and their data interpretation methods for reference and further reading.

Table 11: Electrochemical Noise Data interpretation methods

Analysis Method	Relationship	Description	Reference
Electrochemical Noise Resistance R_n	$R_n = \frac{\sigma_E A}{\sigma_I}$	R_n can be substituted for Polarization Resistance (R_p) and Corrosion Rate (CR) calculated through traditional methods	(ASTM G1, 2003 (2011); ASTM G102, 2010)
Localization Index (LI)	$LI = \frac{\sigma(I)}{rms(I)}$	Index values can indicate localized corrosion	(ASTM G1, 2003 (2011); Ochoa et al., 2001)
Electrochemical Noise Impedance (NI)	$NI = \sqrt{\frac{\varphi_E}{\varphi_I}}$	NI is based on power spectra density (y) of Potential and current and can be related to corrosion rate	(R. A. Cottis, 2001)

When using these interpretation methods both EPN and ECN are used to determine information about corrosion rates and mechanisms.

These methods are difficult to employ in operational environments as they involve sophisticated and sometimes expensive equipment and specially trained personnel for interpretation. A simpler method that could predict when corrosion is occurring in in-situ components without the use of externally applied forces and provide an indication of corrosion amounts would be ideal for ongoing CUI field work. To work towards this goal, a simplified methodology and interpretation scheme was developed. This research is the first step in developing an on-line monitoring system for ongoing CUI field testing and for components (insulated and non-insulated) used in industry.

4.2 Proposed Method

Most field applications involve EN probes placed within the environment of interest recorded data is used to make judgements about the state of the system components (Tan, 2009). Using the components themselves as part of the monitoring scheme would lead to more direct evaluation of system corrosion issues. The following proposed method is the first step in determining the feasibility of this type of condition monitoring for ongoing CUI field work and subsequent application to production components.

As ECN is difficult to measure in the field, a process that employs EPN data alone to make assessment and prediction of corrosion behaviour was developed. One digital multi-meter (DMM) can be used to record multiple sets of EPN information where most ZRAs allow for only one ECN measurement at a time. To build on

this, a simplified data acquisition and analysis method shown in Figure 30 is tested to determine if a reliable correlation between EPN and corrosion rate exists and can be applied in ongoing CUI field applications.

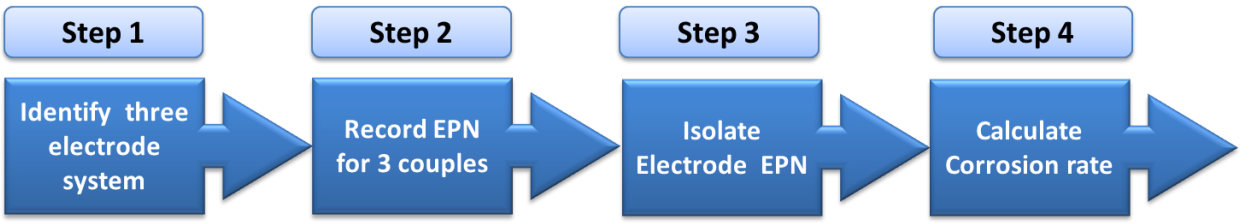


Figure 30: Proposed simplified method to determine corrosion rate from multi-channel electrochemical potential noise measurement.

The first step in this method is to identify three electrodes for monitoring. These three electrodes must be electrically isolated to allow for the measurement of potential difference (V) between electrode couples as illustrated in Figure 28.

In this method a multi-channel DMM is required to facilitate multiple measurements required for Step 2. This allows each electrode to act as the working electrode and specific information about each electrode can be measured. Traditional methodologies measure only one coupled potential and analysis is based on the assumption that three identical electrodes act the same and potential readings are a combination of two equal voltages. For a coupled reading V_{12} the assumption is that V1 = V2 = V and thus electrode potential (V):

$$(V) = {V_{12}(measured)}/{\sqrt{2}} \qquad \text{(Chen \& Gopal, 1999).} \qquad (1)$$

Each voltage measurement (V_{ij}) measures the potential difference between electrodes i and j and a reference electrode k by short circuiting each couple

through internal switching. The three time records of each electrode couple are recorded and analysed further in Step 3.

To isolate each electrode for specific EPN information, the measured potentials (V_{12}, V_{13}, V_{23}) are modified to develop a potential time record of each electrode (V_1, V_2, and V_3).

For a three identical electrode system in same environment:

$$V_{ij} = \left(V_i^2 + V_j^2\right)^{0.5} \qquad \text{(Chen \& Gopal, 1999)} \qquad (2)$$

Applying this to each of the measured electrode couples we have:

$$V_{12} = (V_1^2 + V_2^2)^{0.5} \qquad (3)$$

$$V_{13} = (V_1^2 + V_3^2)^{0.5} \qquad (4)$$

$$V_{23} = (V_2^2 + V_3^2)^{0.5} \qquad (5)$$

Solving for each isolated electrode (V_1, V_2, and V_3) leads to equations 6-8. These equations are then used to isolate each electrode and generate a new time record for each individual electrode.

$$V_1 = \left(\frac{V_{12}^2 - V_{23}^2 + V_{13}^2}{2}\right)^{0.5} \qquad (6)$$

$$V_2 = \left(\frac{V_{12}^2 - V_{13}^2 + V_{23}^2}{2}\right)^{0.5} \qquad (7)$$

$$V_3 = \left(\frac{V_{23}^2 + V_{13}^2 - V_{12}^2}{2}\right)^{0.5} \qquad (8)$$

The final step (Step 4) of the proposed method is to determine the corrosion rate of each electrode based on the isolated EPN (V_1, V_2, and V_3) found in step 3.

EPN and Corrosion rate are related as follows:

Current and potential are related through ohms law

$$Voltage\ (V) = Current(I) \times Resistance(R) \quad (9)$$

For corroding systems

$$I_{corr} = \frac{Potential\ difference}{Total\ Resistance} \quad \text{(Kutz, 2005) so} \quad (10)$$

$$I_{corr} \propto Potential\ difference\ (\Delta V) \quad (11)$$

To account for surface area of the corroding electrode, corrosion current density (i_{corr}) is related to I_{corr} as:

$$i_{corr} = \frac{I_{corr}}{Area} \quad (12)$$

Therefore Potential difference can be related to corrosion current density

$$i_{corr} \propto \frac{Potential\ difference\ (\Delta V)}{A} \quad (13)$$

Corrosion current density is then related to corrosion rate (MR)

$$MR = 8.954\ \times 10^{-3}(i_{corr}) \times EW \quad (14)$$

where MR is the mass loss rate $\left({}^{g}/_{m^2 \cdot d}\right)$ and EW is the equivalent weight of the corroding material. Similar relations can be performed for other variations of corrosion rate such as penetration rate (CR) (ASTM G102, 2010)

$$CR = 3.27 \times 10^{-3} \left(\frac{i_{corr}}{\rho}\right) EW \quad (15)$$

where CR is reported in mm/y.

From the equations above it can be seen that since

$$MR \propto CR \propto i_{corr} \propto \frac{Potential\ difference\ (\Delta V)}{A} \quad (16)$$

and

$$CR \propto \frac{Potential\ difference\ (\Delta V)}{A} \quad (17)$$

It is clear there is a theoretical relationship between EPN and corrosion rate however to fully understand this relationship significant experimental work is needed. To evaluate this simplified method for application in ongoing CUI field testing, a three electrode experimental cell and test plan were completed to verify the EPN/CR relationship.

4.2.1 Experimental

To validate the relationship outlined in step 3 of the simplified method a three nominally identical system was designed and tests completed. The purpose of this experiment is to determine a correlation between isolated electrode potential and

corrosion rate to complete Step 4 of the proposed method shown in Figure 30. To verify the proposed method an expanded process was developed and shown in Figure 31.

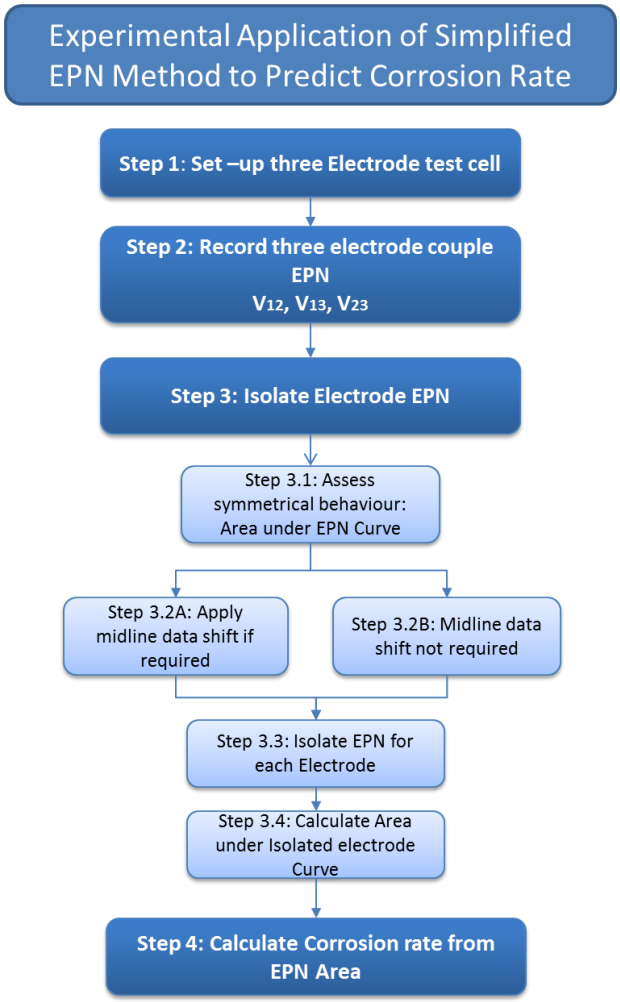


Figure 31: Experimental application of simplified EPN method to predict corrosion rate

Step 1: Set-up three electrode test

The set-up for this experiment consists of three nominally identical electrodes each connected to a positive and negative channel of a Keithley 3700 multi-meter. Built in software was used to program an acquisition pattern to record the coupled

potential of each pair at a measurement rate of 2 seconds. Each voltage measurement (V_{ij}) measures the potential difference between electrodes i and j and a reference electrode k. For the three identical electrode set-up, three voltage measurements are taken, V_{12}, V_{13}, V_{23}. Figure 32 shows the measurement scheme.

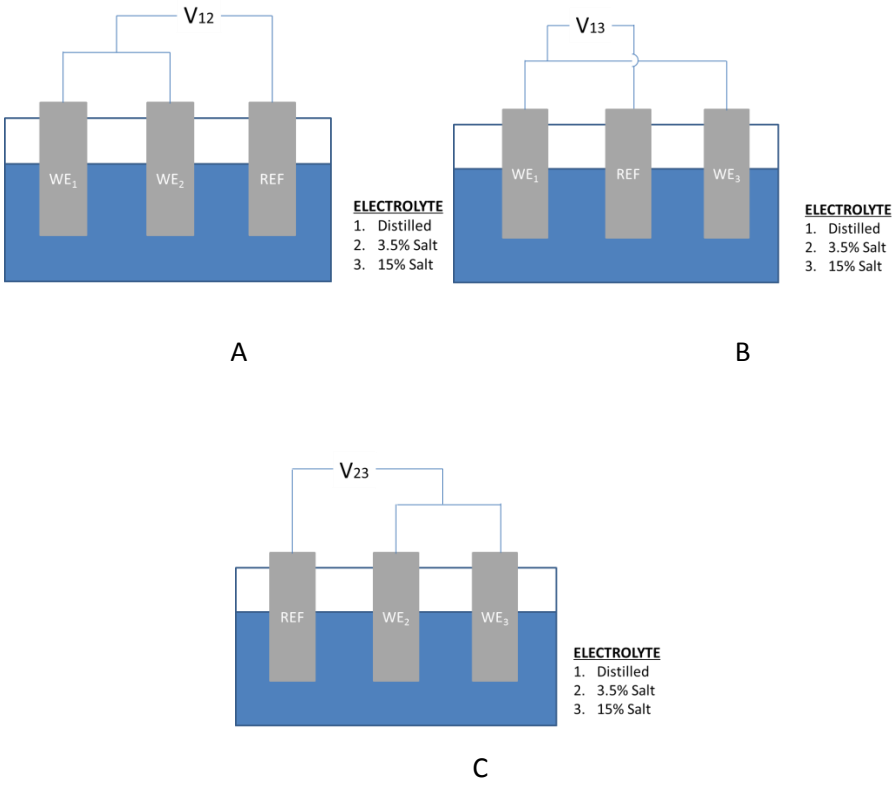
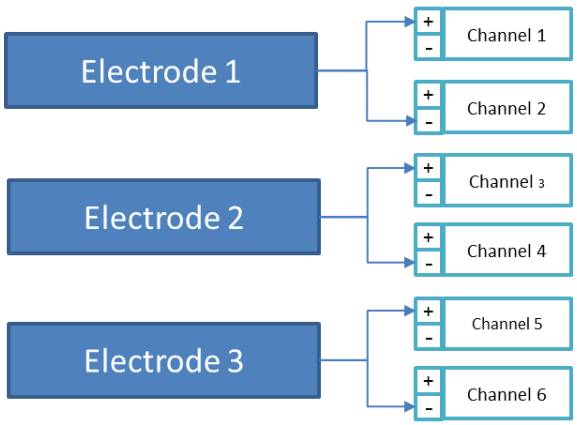


Figure 32: Data acquisition for three electrode system. a) V12 b) V13, c) V23

To measure the set-up shown in Figure 32 on the same three electrodes, a wiring plan was developed to allow for near simultaneous measurements. The electrode connection set-up is illustrated in Figure 33A. The channel pattern shown in Figure 33B for each coupled reading (V_{12}, V_{13}, and V_{23}) records the voltage difference between each short circuited couple (closed positive pair) and the third reference electrode (closed negative).



	V12	V13	V23
Channel 1	C	C	O
Channel 2	O	O	C
Channel 3	C	O	C
Channel 4	O	C	O
Channel 5	O	C	C
Channel 6	C	O	O

C = Channel Closed O = Channel Open

A B

Figure 33: Electrode electrical connection plan for Simplified Method. B. Chanel pattern for recording coupled EPN time records

Three nominally identical plain carbon steel electrodes were prepared according to ASTM G1 (2003 (2011)) with dimensional and mass information recorded. Two factors were used for the experimental plan. Three electrolytes and two time cycles were used with an average exposed surface area of 2068 mm^2. Table 12 outlines each treatment.

Table 12: Experimental plan for testing

Test Run	Treatment	Exposure Time (min)
1	Distilled Water	60
2	Distilled Water	180
3	3.5% NaCl	60
4	3.5% NaCl	180
5	15% NaCl	60
6	15% NaCl	180

All experiments were completed by a single person following the following general procedure for each separate test run:

1. Prepare appropriate electrolyte solution using calibrated balance and cylinder
2. Measure, weigh and label each electrode

3. Connect individual electrode to DMM
4. Secure electrodes to lift device
5. Begin recording data
6. After 5 10 minutes, place electrodes in electrolyte
7. Remove electrode from electrolyte after test exposure time
8. Photograph electrodes
9. Wipe electrodes with acetone
10. Wipe any corrosion product from surface
11. Weigh sample

Details on the completion of laboratory testing is tabulates in Table 13.

Table 13: Experimental details

Test Run	Date	Repeat date	Completed by
1	Jan 11, 2016	Feb 4, 2016	S. Caines
2	Jan 11, 2016	Feb 4, 2016	S. Caines
3	Jan. 13, 2016	Apr. 28, 2016	S. Caines
4	Jan. 20, 2016	Apr. 28, 2016	S. Caines
5	Jan 13, 2016	Aug 30, 2016	S. Caines
6	Jan 11, 2016	Aug 30, 2016	S. Caines

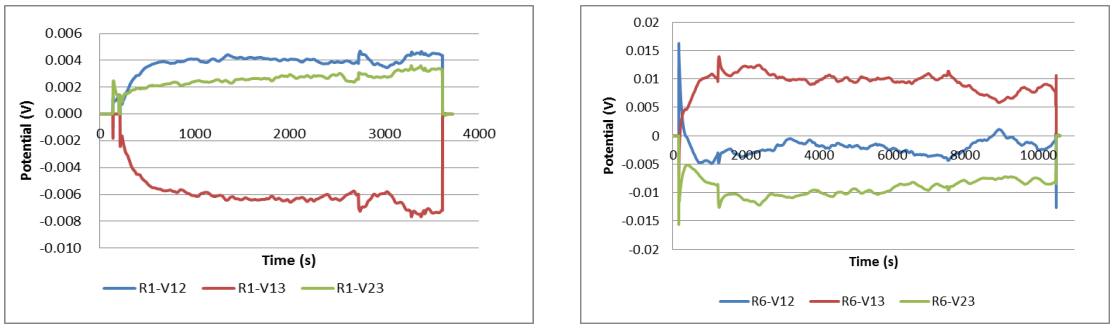
Step 2: Record three electrode couple EPNs

With this new method, all coupled voltages are recorded and analysed (in Step 3 and 4).

Testing indicates that 4 of the 6 test runs demonstrated similar potential profiles. The two test runs (R3, R4 using 3.5% NaCl solution) that did not follow this pattern will be discussed in a later section.

Test runs in 15% NaCl (R5, R6) yielded the highest potential profile and mass loss. These test runs were duplicated to develop additional data and are designated R5B and R6B.

Typical results of distilled water and 15% NaCl tests (R1, R2, R5, R5B, R6 and R6B) demonstrating apparent symmetry in 2 electrode couples are seen in Figure 34. Symmetrical behaviour is noted in V_{12} and V_{13} for test 1 (R1) and V_{13} and V_{23} for test 6 (R6).



A B

Figure 34: Typical EPN-time record data. A: Test 1, B: Test 6.

Step 3: Isolate electrode EPN

To isolate individual electrodes the time records were calibrated to a net zero potential to allow for further comparisons between test runs and individual electrodes. When analysing the area under potential curve (V·s) it can be seen in Figure 35 that the areas are not equal about zero potential.

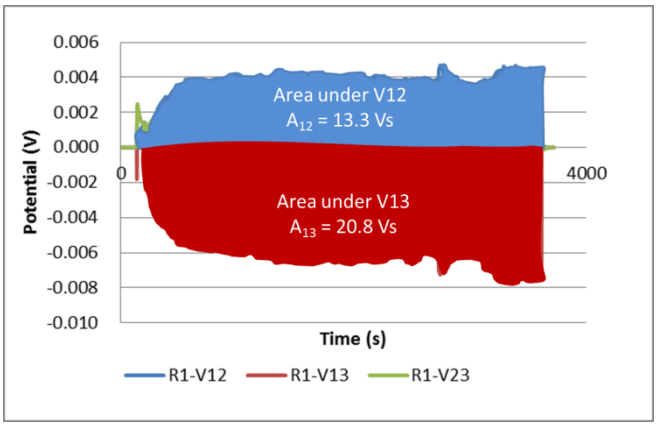


Figure 35: Dissimilar area under voltage curve for test run 1 (R1).

Step 3.2A

To facilitate analysis and electrode comparison the midline between the two symmetrical electrode pair profiles was found and the potential record shifted from the midline to zero potential. Figure 36 shows the calculated midline in step 3.2A used to perform the potential shift.

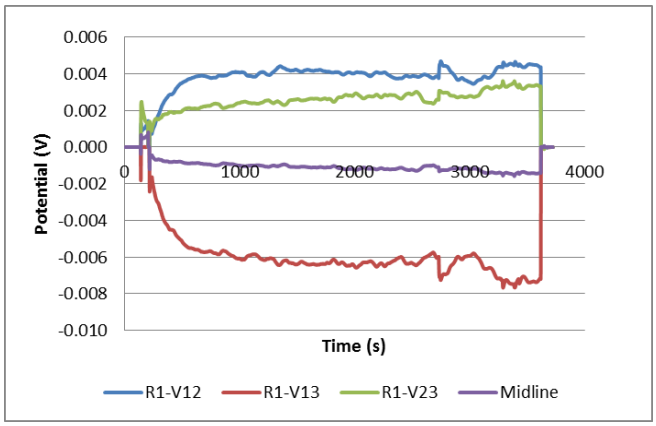


Figure 36: Calculated shift to midline for test run 1 (R1)

As recorded data was then adjusted by shifting from the midline to zero potential resulting in profiles similar to that seen in Figure 37.

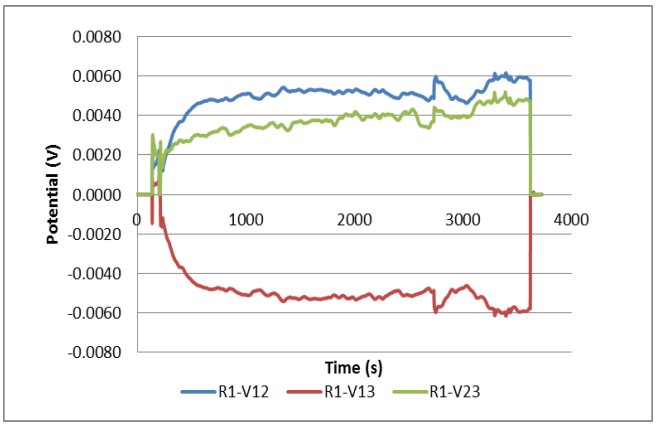


Figure 37: As recorded data adjusted to zero potential midline for test run 1 (R1)

The shift to a zero potential midline allows for easier identification of similar potential area as demonstrated in Figure 38.

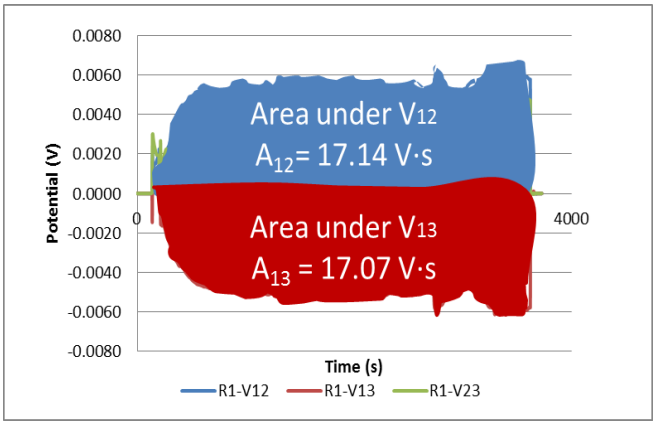


Figure 38: Potential shifted to zero with common area identified for test run 1 (R1).

Step 3.2B

For the 15% NaCl, 3 hour test (R6), symmetry is observed in Figure 39 however application of the midline shift decreased the similarity in potential area (A13 and A_{23}). Table 14 includes these calculated values.

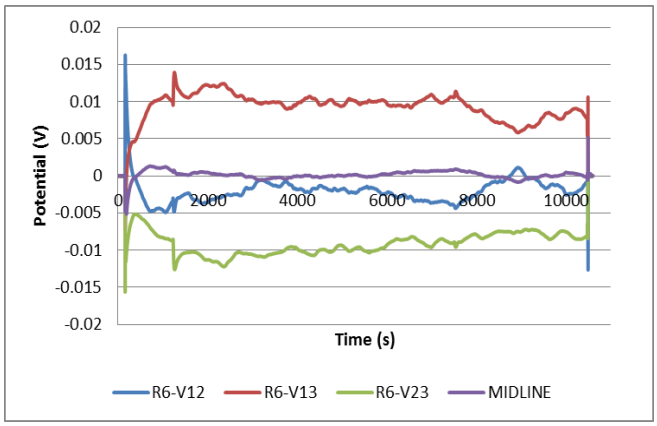


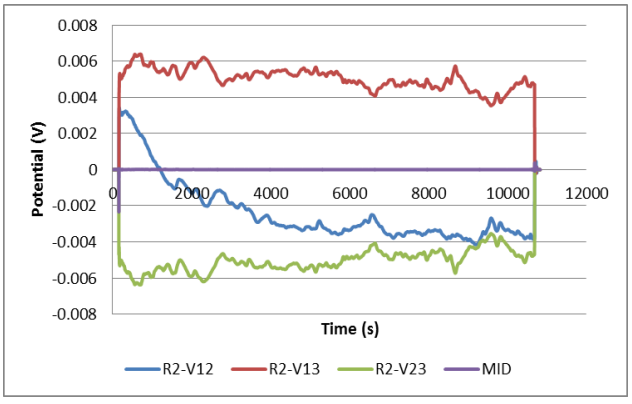
Figure 39: Near zero midline with no shift required

Table 14: Calculated area under the EPN curve values with and without midline shift.

Coupled EPN (R6)	Area under curve:(V·s) No shift in midline	Area under curve:(V·s) Shift in midline
V13	97.3	101.2
V23	94.4	90.4

The non-shifted areas for R6 are closer in value and will be used for further analysis. The recorded data for distilled water, 3 hour test (R2) required no adjustment.

Figure **40** illustrates the near zero midline for the as recorded data of test 2.



A_{13} = 53.3 Vs A_{23} = 53.2 Vs

Figure 40: Recorded data with no midline shift required.

The coupled potential area (A) for each test run is summarised in Table 15. Test runs marked with (*) indicate test results for test runs 3 (R3) and 4 (R4) that are discussed in a separate section.

Table 15: Summarized calculated area under coupled electrode values.

Test Run	A_{12} (V · s)	A_{13} (V · s)	A_{23} (V · s)
1	17.1	17.1	12.8
2	29.1	53.3	53.2
3*	52.1	41.1	38.2
4*	30.8	37.3	23.0
5	14.2	44.7	44.9
5B	12.3	12.0	7.8
6	23.3	97.3	94.4
6B	123.1	137.8	78.6

Step 3.3

The assessment of individual electrodes in step 3.3 of the proposed method determines the contribution of each electrode to the coupled potential measurement and explains inconsistencies such as those observed in Table 14. The symmetrical behaviour seen in test runs 1, 2, 5, 5B, 6 and 6B may indicate that:

1. Two of the electrodes are corroding in a similar manner
2. One of the electrodes is corroding preferentially over the other two electrodes.
3. Combination of 1 and 2

Recorded potential is the potential between the working pair and the reference electrode. To further assess the behaviour of the electrodes and compare electrochemical readings to measured mass loss, information about individual electrodes is needed.

For both distilled water tests and the 1 hour 15% NaCl test (R1, R2, R5, R5B) two of the isolated electrode potentials are very closely aligned with the third electrode showing higher potential. Absolute values of the 1 hour distilled water test (R1) are plotted in Figure 41. Plots of test 2 (R2) and test run 5 (R5 and R5B) demonstrate similar behaviour.

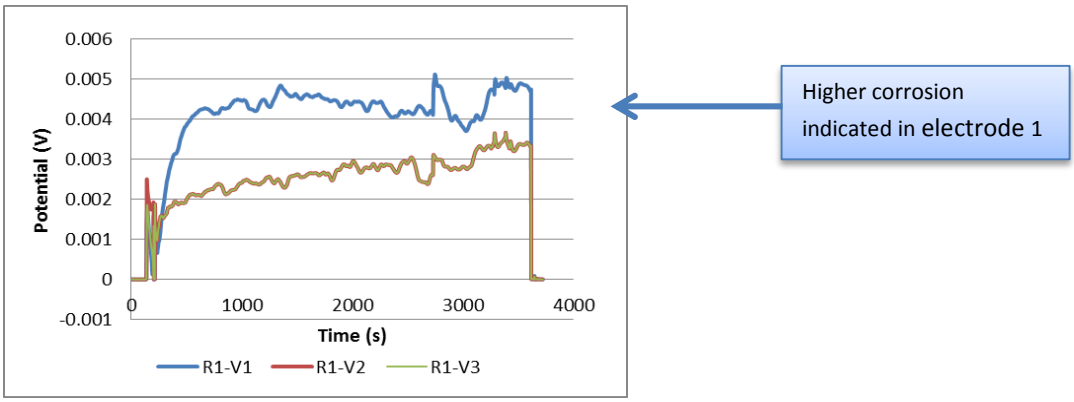


Figure 41: Isolated electrode potential for Test 1

This indicates that one electrode is preferentially corroding over the other two electrodes. As expected, Test 6 (Figure 39 and Figure 42) shows similarity in two electrodes however does not correlate as closely as those in test runs 1, 2, and 5. Similar electrode time records were observed for the second test 6 run (R6B)

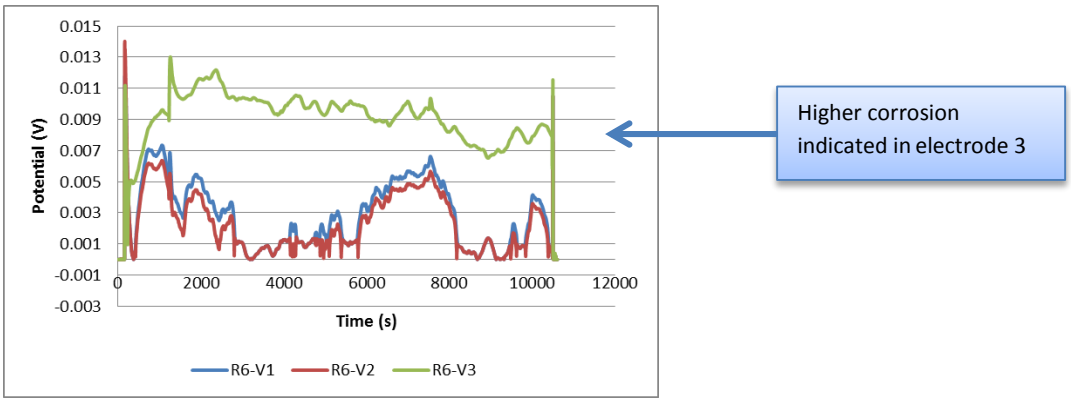


Figure 42: Isolated electrode potential for Test 6

Step 3.4

To quantify the isolated electrode potential, the area under each curve was calculated and is tabulated in Table 16.

.

Table 16: Summary of preferentially corroding electrode indicated from isolated electrode EPN area.

Test Run	Electrode 1 (V·s)	Electrode 2 (V·s)	Electrode 3 (V·s)	Preferentially Corroding Electron
1	14.5	9.1	9.0	Electrode 1
2	20.8	20.4	48.2	Electrode 3
5	42.2	10.3	10.2	Electrode 1
5B	11.2	5.9	5.3	Electrode 1
6	29.8	24.5	95.2	Electrode 3
6B	118.5	37.2	67.7	Electrode 1

To understand the significance of the potential readings, corrosion rates for each electrode are needed.

Step 4: Calculate Corrosion rate

To calculate corrosion rate for comparison with isolated EPN readings mass loss data was generated using standard practises (ASTM G1, 2003 (2011); NACE, 2005). In general terms the mass loss data of test runs 1, 2, 5, 5B, 6 and 6B agreed with what was indicated by the isolated electrode graphs (Figure 43).

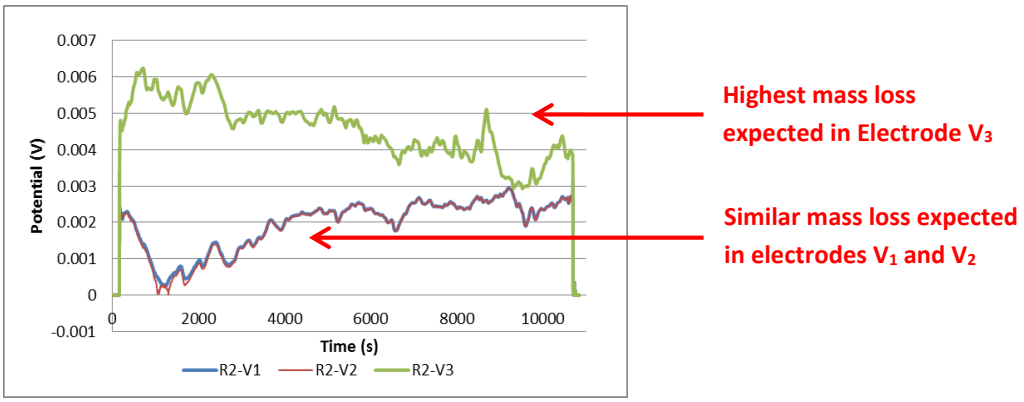


Figure 43 Mass loss expectations for test run 2 (R2)

Mass loss of each electrode was compared to the calculated area under the isolated electrode EPN curve. Figure 44 illustrates the results.

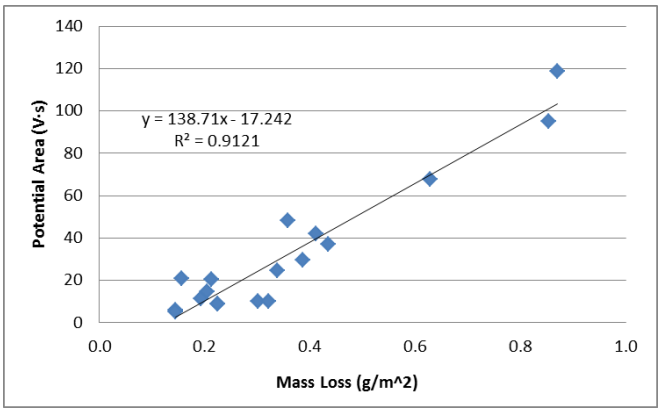


Figure 44: Isolated electrode potential area versus mass loss for R1, R2, R5, R5B, R6 and R6B.

A general linear trend demonstrating increased mass loss with increased potential area can be seen in Figure 44. This is a clear indicator that assumptions of equation 16 are valid.

To complete step 4 of the proposed method, mass loss data is converted to corrosion rate following recommended practice RP0775-2005 (NACE, 2005).

$$CR = \frac{3.65 \times 10^5 W}{A \cdot T \cdot D}$$

where

CR= average corrosion rate in mm/y

W= mass loss in g

A = Exposed surface area of electrode in mm^2

T = exposure time in days

D = density of electrode metal in g/cm^2

The relationship between electrode potential area and calculated average corrosion rate for all distilled water and 15% NaCl test runs (R1, R2, R5, R5B, R6, and R6B) is graphed in Figure 45. A single relationship was not indicated.

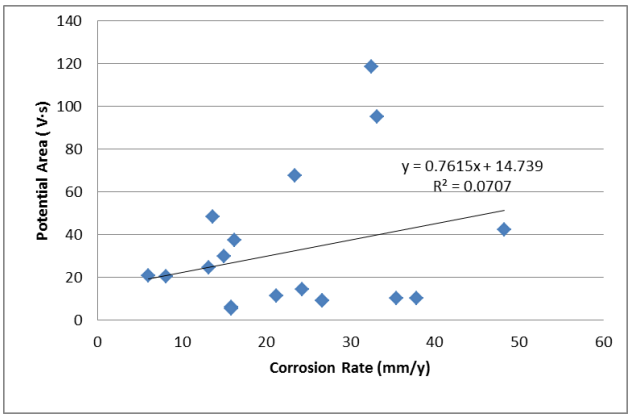


Figure 45: Calculated corrosion rate comparison to potential area for test runs R1, R2, R5, R5B, R6 and R6B isolated electrodes.

Further analysis comparing corrosion rate to mass loss data indicates the source of the undefined relationship. Figure 46 shows a comparison between mass loss and corrosion rate. Again, no single relationship exists for all data.

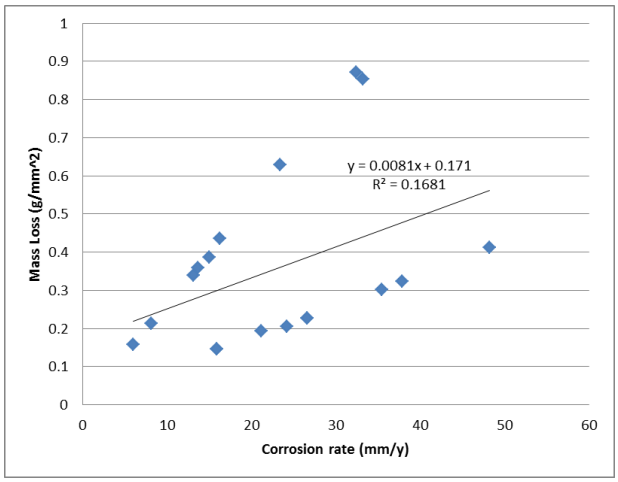


Figure 46: Mass loss compared to corrosion rate for R1, R2, R5, R5B, R6 and R6B isolated electrodes.

When all data was considered together no trend was found however two separate trends were observed. Figure 47 shows separate trend lines for 1 hour immersion tests (R1, R5 and R5B) and 3 hour immersion tests (R2, R6 and R6B).

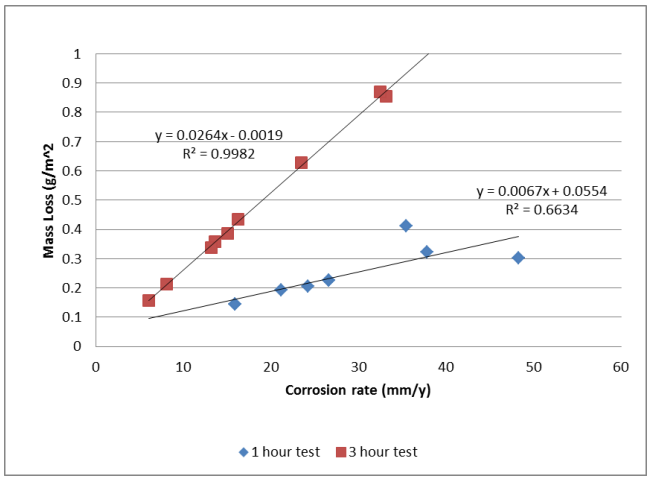


Figure 47: Mass loss compared to corrosion rate for R1, R2, R5, R5B, R6 and R6B isolated electrodes. Trends for 1 hour test electrodes and 3 hour test electrodes identified.

When viewed separately good correlation (R^2 =0.9982) is found for the three hour tests with less clear trend (R^2=0.6634) for the shorter duration tests.

Re-examination of Figure 45 for separate trends for 1 hour and 3 hour immersion times show correlated relationships between potential area and corrosion rate. These trends are shown in Figure 48.

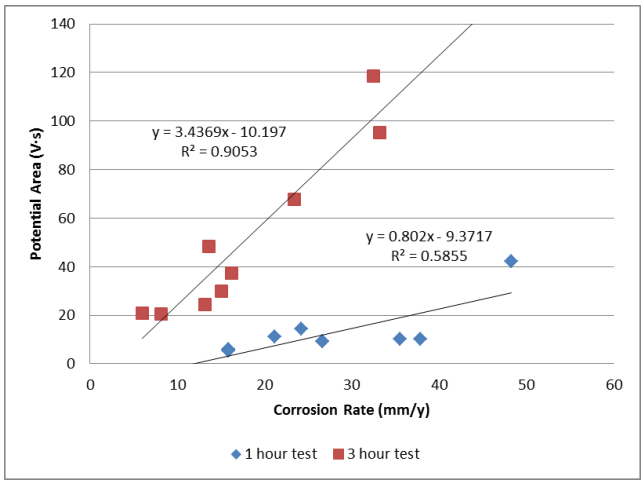


Figure 48: Calculated corrosion rate comparison to potential area for R1, R2, R5, R5B, R6 and R6B isolated electrodes. Trends for 1 hour test electrodes and 3 hour test electrodes identified.

4.2.1.1 Application of proposed Method to Test Runs 3 and 4 (3.5% NaCl)

Tests R3 and R4 (3.5% NaCl) did not closely follow the pattern of other tests (R1, R2, R5, R5B, R6 and R6B) and did not indicate a clear symmetrical profile.

Due to this inconsistency, duplicate runs (R3B and R4B) with 3.5% NaCl were run to determine if unexpected results were due to experimental error or a fundamental difference in behaviour at 3.5% NaCl. The second run at 3.5% NaCl (R3B and R4B) were also not consistent with the pattern of the distilled water and 15% NaCl tests (R1, R2, R5, R5B, R6 and R6B) however they did demonstrate similar patterns as the first 3.5% NaCl tests. Typical coupled time data (V_{12}, V_{13}, V_{23}) for 3.5 % NaCl tests are shown in Figure 49

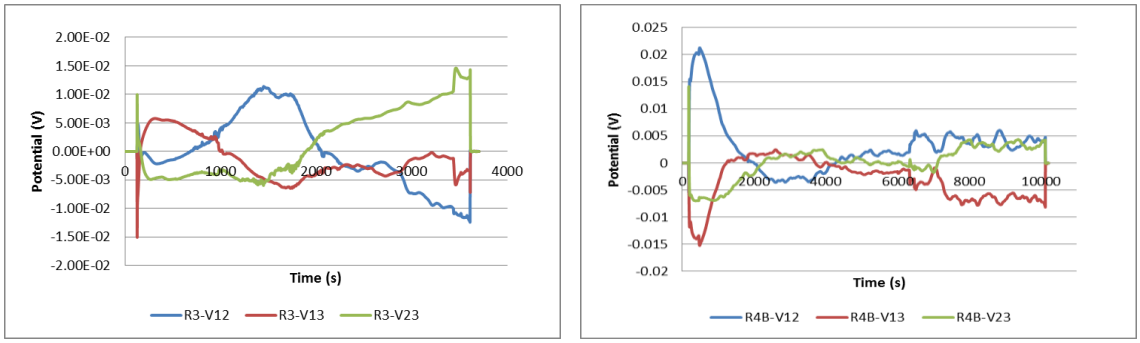


Figure 49: Typical coupled potential for 3.5% NaCl tests

The coupled EPN were isolated using the equations in Step 3 (equations 6-8) and the results presented in Figure 50.

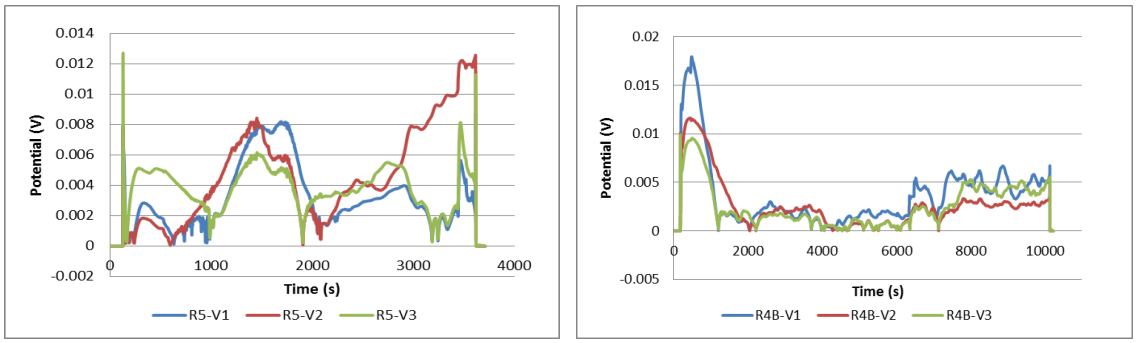


Figure 50: Isolated electrode potential of R3, R3-B, R4, and R4-B

In general all electrodes involved in the 3.5% NaCl solution demonstrate increased fluctuations in the potential time record compared to the other solutions (distilled water and 15% NaCl).

Electrode mass loss was compared to area under the isolated electrode area for all 3.5% NaCl tests and the results tabulated in Table 17 and graphed in Figure 51.

Table 17: Isolated electrode mass loss data for 3.5 % NaCl, initial runs = R3 and R4, Re-Run = R3B and R4B

Electrode	Mass Loss (g/ m^2)	Area under Potential Curve (V·s)
R3-1	*3.59	11.36
R3-2	0.749	16.68
R3-3	0.60	13.52
R3B-1	0.48	38.18
R3B-2	0.48	41.11
R3B-3	0.34	52.08
R4-1	*-86.17	44.95
R4-2	0.69	80.63
R4-3	0.59	41.51

R4B-1	0.19	37.01
R4B-2	0.00	26.74
R4B-3	0.34	26.06

From the information presented in Table 17 two results are identified as possible outliers, Electrode 1 from the initial Run 3 (R3-1) and electrode 1 from initial Run 4 (R4-1). There are two suspect values so the Grubbs test is applied (AMCTB No 69, 2015).

$$G = \frac{(x_n - x_1)}{s} \tag{18}$$

For this sample set

$$G = \frac{(3.588 - (-86.1702))}{24.0347} = 3.7345 \tag{19}$$

The high value of G considering both data points clearly indicates both data points as outliers and are not included moving forward.

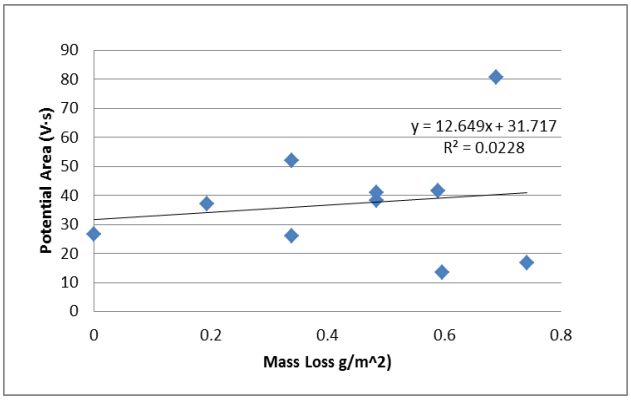
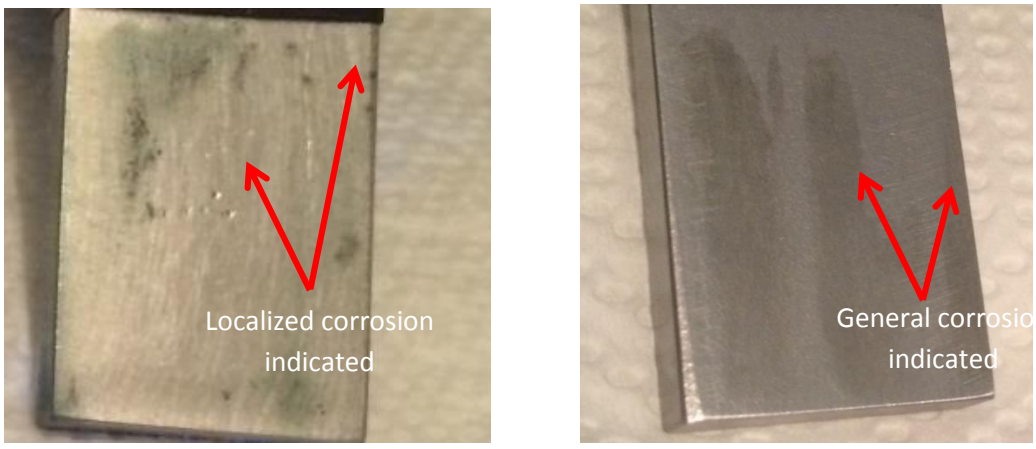


Figure 51: Graph of mass loss vs potential area for 3.5% NaCl Tests R3, R3B, R4, R4B with outliers removed

With the two outliers removed, Figure 51 does not indicate a clear linear relationship as that observed in the distilled water and 15% NaCl tests.

While the 3.5% NaCl tests (R3, R3B, R4 and R4B) did not show strong correlation, the difference in behaviour from all other tests (R1, R2, R5, R5B, R6, R6B) indicate there are likely different mechanisms involved. Examination of surface corrosion indicates possible localized corrosion with 3.5% NaCl. Representative surfaces are shown in Figure 52.



A B

Figure 52: Surface condition of electrodes after testing. A. Electrode from Initial 3.5% NaCl Test run 4 (R4-3) B. Electrode 3 from 15% NaCl test run 8 (R8-3)

When the second 3.5% NaCl test data is included in the mass loss correlation graph with all other tests (R1, R2, R5, R5B, R6, R6B) a linear trend can still be seen in Figure 53. This indicates that while there appears to be an unknown phenomenon affecting corrosion behaviour at 3.5 % NaCl, the underlying theory of this work is still applicable.

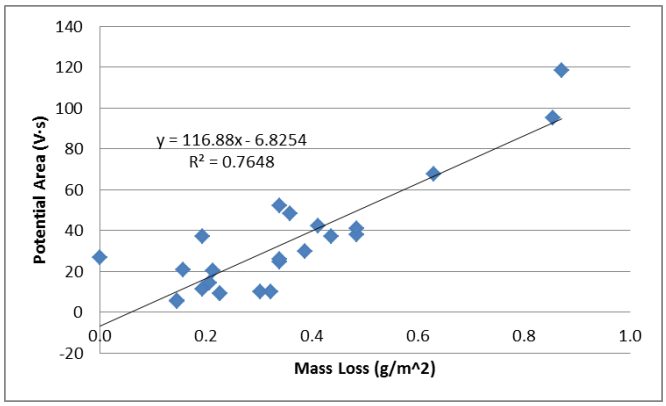


Figure 53: Complete test run data (R1, R2, R3B, R4B, R5, R5B, R6, R6B) indicating linear trend.

Inclusion of the 3.5% NaCl test runs R3B and R4B when comparing corrosion rate and potential area for each immersion time (Figure 54) shows a stronger correlation for longer immersion times than shorter immersion times.

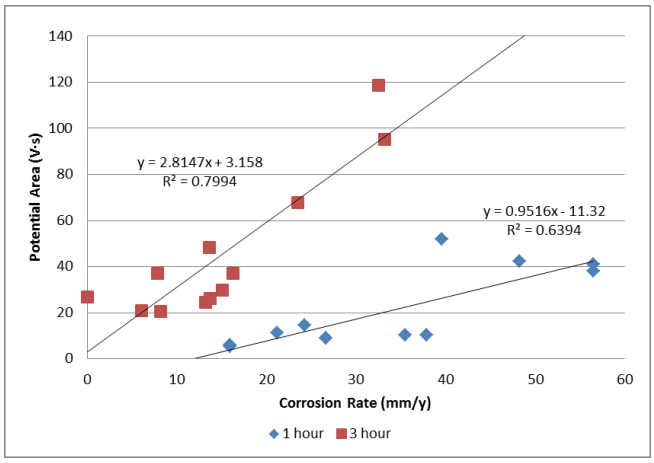


Figure 54: Corrosion rate comparison to potential area for R1, R2, R3B, R4B, R5, R5B, R6, and R6B isolated electrodes. Trends for 1 hour test electrodes and 3 hour test electrodes identified.

4.3 Discussion

4.3.1 Mass Loss Data:

The noted inconsistencies with mass loss data can be explained by the inherent issues with short term corrosion testing. With short term testing the mass loss experienced is very small and any issue with the cleaning process can result in inconsistent data that can greatly influence correlation. The presence of localized corrosion may explain the lower than expected mass loss in some electrodes as corrosion product of localized corrosion is more difficult to remove. As the mass loss expected is small, even little retained corrosion product can have a significant impact on total mass loss recorded. One way to combat this issue is to increase the immersion times to increase the overall mass loss and reduce the impact of any issues with sample cleaning.

4.3.2 3.5% NaCl :

The unexpected results from the 3.5% NaCl tests can be explained by changes in the corrosion mechanism from uniform to localized corrosion. Examination of the time records of the 3.5% NaCl test runs in

Figure 50 indicate that these electrodes experienced greater variation in potential.

To further explore this, one electrode from each of the three hour test runs (R2, R4B, R6) were analysed further. Electrodes with the highest cumulative potential

readings were chosen and a comparison of these individual electrodes is shown in Figure 55.

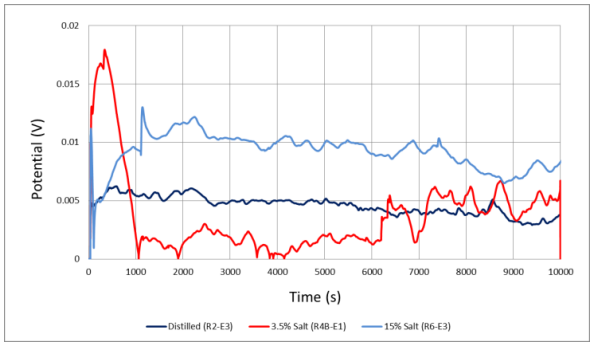


Figure 55: Isolated electrode comparison for three hour immersion tests. Electrode with the maximum cumulative potential selected for comparison,

This figure illustrates the overall trend for the 3.5% NaCl test electrode (R4B-E1) is lower than the potential curves for distilled and 15% NaCl tests, however the electrode potential shows more variation. Increased variation in the potential/time record can indicate localized corrosion as introduced in Figure 29.

To quantify this variation, the standard deviation of each electrode was found for a moving sample size of 100. Figure 56 shows the standard deviation of the selected isolated electrodes.

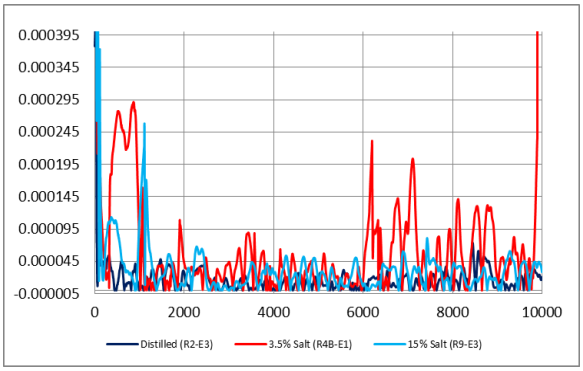


Figure 56: Standard deviation of isolated electrode potential for select electrodes in three hour test runs R2, R4B, and R6

Higher variation in the 3.5% NaCl electrode (R4B-E1) can be easily seen and further confirms the likelihood of localized corrosion in the 3.5% NaCl tests.

4.3.3 Corrosion Rate and Immersion Time

Corrosion rate based on mass loss data is an average corrosion rate and assumes stability over time. This is not the case in practice. Many works demonstrate that corrosion rate changes with time and that while corrosion loss (mass loss) increases with time; the rate of loss (corrosion rate) decreases (Melchers & Jeffrey, 2008; Oparaodu & Okpokwasili, 2014; Winston Revie (ed), 2011). For this experiment this phenomenon can be seen in Figure 47. For shorter immersion times, mass loss is low with a high corrosion rate where the longer immersion time electrodes show higher mass loss with lower corrosion rates.

4.3.4 Overall method

The four step method introduced in Figure 30 was successfully applied to short run tests and a relationship between isolated electrode EPN and both mass loss and corrosion rate were established. The ability to make direct predictions about individual electrodes rather than an electrode pair allows for dissimilar corrosion behaviour in the electrodes to be examined and indicates that the requirement for identical electrodes may be avoided for field work. Application of Step 3 to dissimilar electrodes can allow for the expansion of this method to in-service components where the identical electrode restriction is not possible.

This new simplified method uses measured potential alone in Step 4 to calculate the likely corrosion rate of a component. The agreement of both distilled water tests and 15% NaCl tests indicate that this method can be applied directly without full knowledge of the corrosion conditions. Application of this method in uncontrolled field conditions requires this relationship to allow for unknown concentrations in the corrosion environment.

The results of this study indicate that the simplified method can be used to indicate CUI rate and mechanism in field applications. The simplified method will be applied to the long term data generated from the authors concurrent CUI field studies (Caines et al., 2015).

4.3.5 Next Steps

To fully develop this simplified method for expanded application additional testing is required to characterize the relationship between isolated electrodes and their EPN. Future work includes:

- Longer term testing: required to characterise the EPN / CR relationship. Issues with the impact of retained corrosion product can be reduced with longer term testing where increased mass loss is expected.
- Dissimilar electrodes test: Required to validate the application of the method for non-identical electrodes. This will expand the application of the simplified method to the field applications

- Apply to CUI: Application of this method to lab scale CUI tests needed to both quantify the increased corrosion observed in components under insulation and to further develop the simplified method for field applications.

- Determine accuracy and reliability of the proposed method through evaluation of environmental disturbation.

$$Err = \sqrt{\frac{(V_1 - V_2)^2 + (V_2 - V_3)^2 + (V_1 - V_3)^2}{3}}$$

4.4 Conclusions

This new simplified method uses a multichannel digital multi-meter to record near simultaneous potential couple measurements to allow for the isolation of individual electrode potential- time profiles. The method uses these isolated electrode EPN records to predict corrosion rate of each individual component. A relationship between isolated electrode EPN, mass loss and corrosion rate was established and the method demonstrated as a promising way to monitor corrosion with further development. Key conclusions for this work include:

- New methodology allows for individual comparison of electrode potential, mass loss, and corrosion rate.

    - Traditional techniques analyse couple potential and assume identical behaviour of coupled electrodes.

    - Results from testing indicate individual electrodes do not behave identically.

- Distilled water and 15% NaCl solution tests showed a relationship between individual electrode potential area and mass loss.
    - Longer term testing should be conducted to confirm relationship and determine probability relationship.

- Distilled water and 15% NaCl solution tests showed a relationship between individual electrode potential area and corrosion rate.
    - Corrosion rate relationship is time dependant and correlation found when similar immersion time were analysed together.

- EPN for 3.5% NaCl test run electrodes did not correlate as well as the other tests solutions.
    - These electrodes likely experienced localized corrosion as indicated by increased variation in the EPN readings.
    - Low overall mass loss increased the impact of retained corrosion product and explains the unexpected apparent inconstant behaviour of these tests.

- Longer immersion times showed better correlation.

This research validates that a relationship between isolated EPN and corrosion rate exists and demonstrates the simplified method can be used to collect data on multiple electrodes. This method will be applied to the long term data generated from the authors concurrent CUI field studies and should be pursued as a potential monitoring technique for in-situ applications.

Index of Terms

A Current

AE Axillary electrode

CR Corrosion Rate

CUI Corrosion Under Insulation

DMM Digital multi-meter

ECN Electrochemical Current Noise

ER Electrical resistance

EN Electrochemical noise

EPN Electrochemical Potential Noise

EW Equivalent weight

LPR Linear Polarization resistance

MR Mass loss rate

RE Reference Electrode

RFID Radio-frequency identification

SCE Saturated calomel electrode

V Potential

WBE wire beam electrode

WE Working Electrode

ZRA Zero resistance ammeter

4.5 References

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5.0 Demonstration of increased corrosion activity for insulated pipe systems using a simplified electrochemical potential noise method

Preface

A version of this paper is currently in the peer review process in the Journal of Loss Prevention in the Process Industries (as of November 2016). Susan Caines is the primary author for this work. Co-authors for this manuscript include Dr. Faisal Khan and Dr. John Shirokoff. The primary author developed the conceptual model, the design of experiments, experimental design, completed experiments, results and analysis and prepared the first draft of the manuscript. The co-author Faisal helped in developing the concept, experimental setup and testing of the concepts, reviewed and corrected the models and results, and contributed in preparing, reviewing and revising the manuscript. Co-author Dr. John Shirokoff contributed through support in the development and improvement of the design and assisted in reviewing and revising the manuscript.

Abstract

Corrosion under insulation (CUI) is a significant issue in industry. When a component is insulated, moisture could become trapped at pipe surfaces and lead to corrosion. The severity of corrosion under insulation could be considered greater than a component without insulation in a similar environment. This belief

has not yet been demonstrated or reported in the literature. To understand CUI the difference in systems under insulation and systems without insulation must be determined to confirm the anecdotally held understanding that corrosion can be more severe under insulation. Experiments were conducted to demonstrate the difference in corrosion severity of pipe surfaces exposed to insulation and surfaces without insulation. Increased mass loss and corrosion rates were found for electrodes under insulation over electrodes without insulation. The increase in corrosion was found using a simplified electrochemical potential noise (EPN) method and confirmed through visual observation and mass loss data.

5.1 Introduction

Corrosion under insulation (CUI) is a difficult and persistent problem that affects many operations. CUI occurs on the surface of a component that is covered by insulation. Insulation is used for many different reasons, most commonly to protect personnel from extreme surface temperatures and to regulate process temperatures. Insulation is integral to the safe and economical operation of industrial components and use cannot be eliminated.

Because the surface is covered from view, detecting CUI is difficult and costly. Visual inspections are only possible through expensive removal of insulation and in most operations the amount of insulation installed makes this prohibitively expensive for routine maintenance plans (Caines, Khan, & Shirokoff, 2013). Alternative non-destructive evaluation methods are available however, again the

volume of insulated pipes and components make inspection of all prohibitively expensive. In the offshore industry, standards and recommended practices (API 579-1/ASME FFS-1, 2007; ASME B31.G, 2012; BS 7910, 2005; DNV-RP-G101, 2002; FITNET, 2006) are used to predict and plan inspection and maintenance schedules. While theses methodologies are comprehensive and widely used in the offshore industry, they do not fully specify corrosion rates under insulation and the user is required to provide specific corrosion rates when following the recommended practises and guide lines (Caines et al., 2013).

Corrosion on surfaces exposed to harsh marine environments (non-insulated) is not completely understood as the mechanisms and causes for corrosion initiation and propagation are stochastic and as such cannot be predicted with certainty (Caines et al., 2013; Davis, 2000; European Federation, Institute, Winnik, & Institute, 2008; Roberge, 2008). There are rates and methods for predicting behaviour of exposed pipe surfaces that allow operators to choose proper materials for components and plan inspection and maintenance schedules (DNV-RP-G101, 2002; Melchers, 2003; Melchers & Jeffrey, 2008; Roberge, 2008; Svintradze & Pidaparti, 2010). The question becomes are these rates of corrosion and predictive measures developed for non-insulated assets applicable to components under insulation?

The first step in understanding and predicting the behaviour of CUI is to understand the effect of insulation on the corrosion behaviour. Rates and methods developed for uninsulated materials cannot be directly applied to insulated pipeline without

study as the environmental set-up is different and conditions for corrosion are significantly different. Insulation is designed to keep moisture away from the surface however if moisture does penetrate the system, this design feature limits any opportunity for the moisture to escape. The reason for moisture introduction in the annular space is a complicated issue that is beyond the scope of this work but this issue is vital to understanding CUI and to developing future preventative strategies.

If a non-insulated pipe becomes wet from rain or the like, there is limited opportunity for the moisture to become trapped and create corrosion conditions at the surface. Ideally, insulated pipe surfaces are protected from moisture however this is not always possible in practice. Once moisture is introduced under the insulation, the moisture can become trapped as demonstrated in Figure 57.

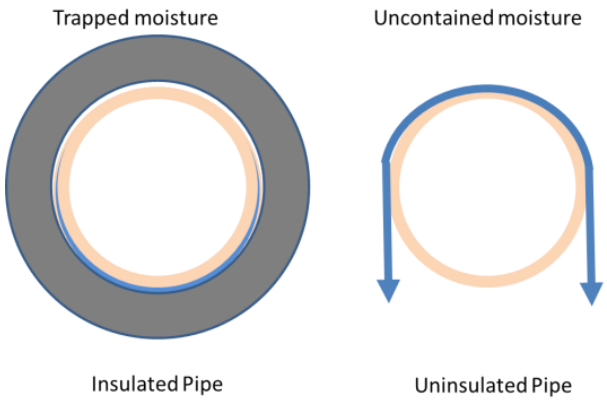


Figure 57: Demonstration of differences in insulated and uninsulated pipe

To assess the corrosion behaviour in these different configurations traditional mass loss evaluation alone is not sufficient to characterise the effects of insulation.

Electrochemical methods are available to assess the corrosion behaviour of materials. Linear polarization resistance (LPR), electrical resistance (ER), and electrochemical noise (EN) can be used in corrosion assessments. Linear polarization uses an input potential and measures the resulting current between corroding electrodes. This relationship, Rp, is inversely proportional to the rate of corrosion (Yang, 2008). Electrical resistance measures the change in electrical resistance due to surface changes from corrosion damage. This method is generally used as ER probes to monitor likely corrosion in an environment (Bertocci, Huet, & Nogueira, 2003; Naing, Wong, & Yong-Jun Tan, 2006). These probes are placed in the environment of interest and the ER rates of the probe material are translated into corrosion rates for the components themselves. Electrochemical noise methods monitor the naturally occurring fluctuations in current and potential. This is a passive technique that does not require the external input required for LPR and ER.

To evaluate the naturally occurring CUI in piping systems EN methods are desirable over LPN as EN methods do not apply any outward disturbance to the system under study allowing for direct measurement of corrosion. ER Probes may create changes in geometry of the annular space between the pipe surface and insulation possibly leading to increased corrosion around probe site where EN methods can be applied directly to the pipe surface.

As part of an overarching research plan to study CUI in laboratory and field conditions (Caines, Khan, Shirokoff, & Qiu, 2015), the authors developed a

simplified electrochemical noise method to record changes in the naturally occurring potential difference (EPN) between two electrodes (Caines, Khan, Zhang, & Shirokoff, 2016). This simplified method uses a traditional three nominally identical electrode set-up. Unlike traditional three electrode systems that measure the EPN between two of the three electrodes, the simplified method measures the EPN of all electrode pairs to allow for isolation of each electrode. With this simplified method the potential of each individual electrode was found from the coupled time records and it was demonstrated that the relationship between mass loss rate (corrosion rate (CR)) and EPN is proportional. Figure 58 outlines the steps developed by Caines et al (2016) for the simplified method of using EPN to estimate corrosion rate.

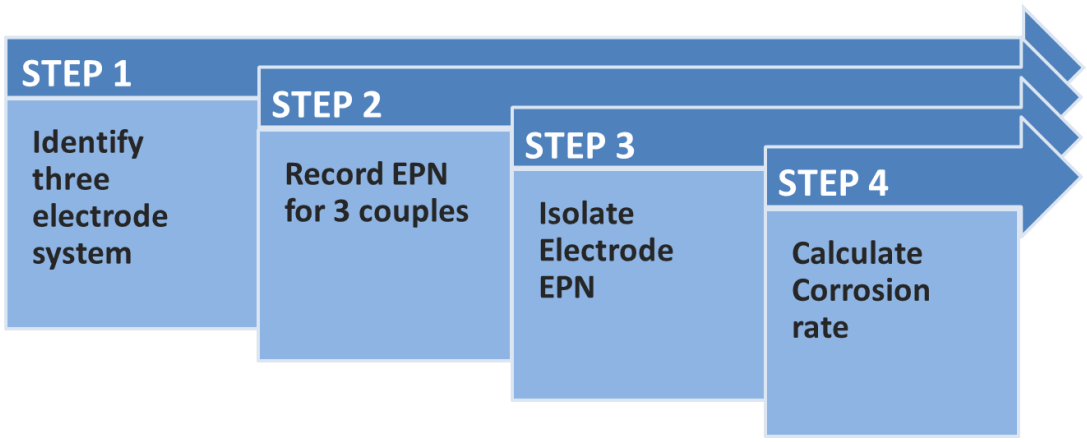


Figure 58: Simplified EPN method (Caines et al., 2016) to evaluate isolated electrode potential for evaluation of the effect of insulation on the corrosion behaviour of pipe surfaces.

This method modifies a traditional three nominally identical electrode set-up (step 1) to measure coupled EPN data for all electrodes (step 2). Figure 59 illustrates this set-up for measuring the coupled EPN (V_{ij}) for one electrode pair (E_i & E_j)

against the third electrode (E_k) acting as a reference electrode. This measurement is duplicated for all electrode pairs (E_i & E_k and E_j & E_k) to measure the corresponding coupled EPN (V_{ik} and V_{jk}).

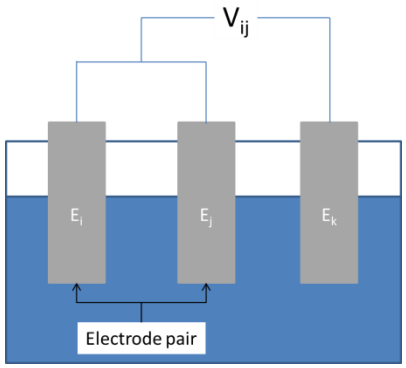


Figure 59: Electrode set up measuring coupled EPN for Caines et al (2016) Simplified EPN Method.

After all coupled electrode EPN is recorded, this data is then separated into individual EPN data for each individual electrode (step 3). This step uses equations 20-22 developed by Caines et al (2016) to isolate EPN information for each individual electrode.

$$V_i = \left(\frac{V_{ij}^2 - V_{jk}^2 + V_{ik}^2}{2}\right)^{0.5} \quad (20)$$

$$V_j = \left(\frac{V_{ij}^2 - V_{ACik}^2 + V_{jk}^2}{2}\right)^{0.5} \quad (21)$$

$$V_k = \left(\frac{V_{jk}^2 + V_{ik}^2 - V_{ij}^2}{2}\right)^{0.5} \quad (22)$$

where i, j, and k represent individual electrodes in a three electrode system.

In step 4 the corrosion rate of each electrode is estimated by the individual EPN data for each electrode. The relationship between EPN and corrosion rate was verified by Caines et al (2016) through comparison to individual electrode mass

loss data. Ongoing work is needed to determine precise relationships to complete this step and provide a direct link between recorded individual EPN and a reliable corrosion rate.

To better understand, predict and quantify the differences in insulated and non-insulated components, a side by side comparison experimental plan was developed. This paper outlines the methodology and results of this study. Through application of the simplified electrochemical method the differences in these situations can be quantified and an increased understanding of the potential risks associated with the application of insulation can have on operations. This work will also further demonstrate the usefulness of the simplified electrochemical noise methodology proposed by Caines et al (2016).

5.2 Experimental set-up

To study the effects of insulation on piping systems, an experimental set-up was designed and constructed. This set-up allows for direct comparison of the corrosion on pipe surfaces of both insulated and non-insulated systems. The set-up for both systems (insulated and non-insulated) is based on the ASTM standard G186 Standard Guide for Laboratory Simulation of Corrosion under Insulation (2013). This standard recommends the use of either or both mass loss data and linear polarization resistance (LPR) methods to assess CUI. Based on this standard, a six electrode system was designed. LPR methods were replaced by the new simplified EPN method created by Caines et al (2016) to take advantage

of the passive nature of the technique. Each unit includes two separate three electrode systems (sides A and B seen in Figure 60). The potential of each electrode pair was measured using a Keithley 3700A digital multi-meter (DMM). This measuring scheme can be seen in Figure 60 and Table 18.

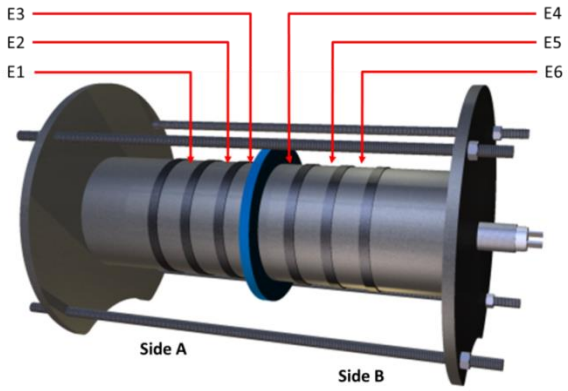


Figure 60: Experimental set-up for evaluation of the effects of insulation on piping systems.

Each electrode is connected to the DMM and switching is used to measure the potential between each coupled (short circuited) pair and the third electrode acting as a reference.

Table 18: Measurement scheme of electrode couples. X indicated electrode pairs

		Coupled EPN (Measured)											
		Insulated						Non-Insulated					
		Side A			Side B			Side C			Side D		
	Electrode	V_{12}	V_{13}	V_{23}	V_{45}	V_{46}	V_{56}	V_{78}	V_{79}	V_{89}	V_{1011}	V_{1012}	V_{1112}
Insulated	E1	X	X										
	E2	X		X									
	E3		X	X									
	E4				X	X							
	E5				X		X						
	E6					X	X						
Non-Insulated	E7							X	X				
	E8							X		X			
	E9								X	X			
	E10										X	X	
	E11										X		X
	E12											X	X

For the insulated set-up (Figure 61), insulation is fitted around each side of the unit and sealed to allow electrolyte entrapment in the annular space created by the insulation. Liquid inlet and outlets are installed to provide access for electrolyte.

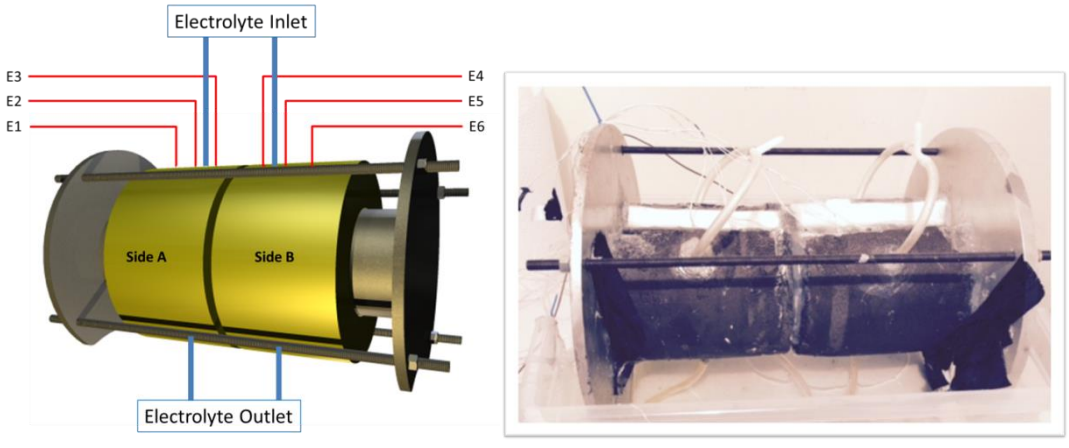


Figure 61: Insulated experimental set-up (Schematic and Actual)

For the un-insulated set-up, the unit is fitted with a custom designed trough to allow for controlled wetting of the pipe surface similar to that introduced under insulation. For the non-insulated set-up, liquid is introduced to the trough with a funnel and removed through outlet piping at the bottom of the trough. In this set-up there is no opportunity for liquid entrapment as the electrolyte is drained from the trough and be visually confirmed during testing (Figure 62).

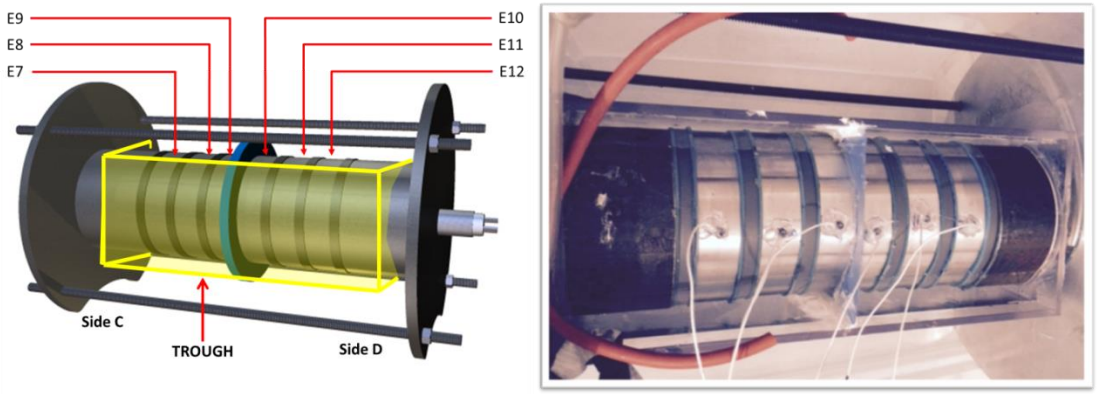


Figure 62: Un-insulated experimental set-up (Schematic and Actual)

Together these experimental set-ups allow for direct comparison of the effect of insulation on the corrosion of the pipe surface.

5.3 Experimental plan

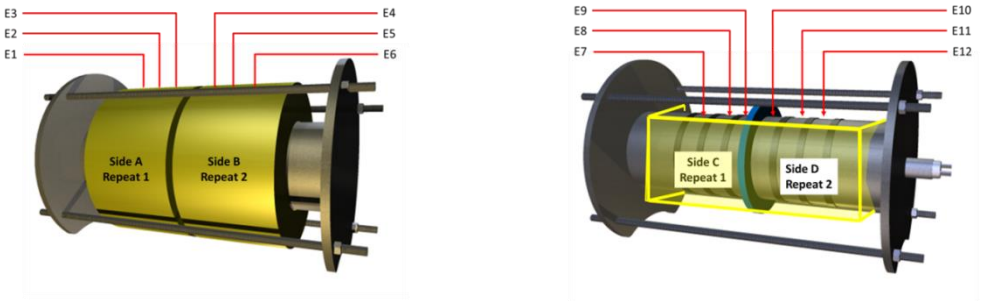
An experimental plan was designed to examine the effects of insulation on pipe surface corrosion. The cyclic nature of moisture at pipe surfaces is included in the experimental plan. Each test includes three cycles of wettings of the pipe surface followed by timed dry periods.

The experimental plan includes three factors (insulation, dry time and electrolyte) each at two levels. This plan requires the eight experimental treatments shown in Table 19.

Table 19: Experimental plan

Test	Treatment	Insulation	Dry time	Electrolyte
1	A	Y	1 hr	Distilled water
	B	N	1 hr	Distilled water
2	C	Y	1 hr	Seawater
	D	N	1 hr	Seawater
3	E	Y	8 hr	Distilled water
	F	N	8 hr	Distilled water
4	G	Y	8 hr	Seawater
	H	N	8 hr	Seawater

Each treatment (A-H) is repeated during each test with two separate experimental units. These repeats can be seen in Figure 61. Two treatments are included in each test shown in Table 19. For each test, one insulated unit and one non-insulated unit are included.



Treatment	Test	Treatment
A	1	B
C	2	D
E	3	F
G	4	H

Figure 63: Experimental plan including repeats and treatments.

To complete the experimental plan, 16 separate groups of data were collected. Treatment A includes insulation with distilled water electrolyte and a 1 hour drying time. For this treatment, six (6) individual data sets are recorded. For side A (repeat 1) three coupled EPN values are recorded (V_{12}, V_{13}, V_{23}). For side B (repeat 2) three additional EPN values are recorded (V_{45}, V_{46}, V_{56}). Table 20 demonstrates the data groups collected for all tests and treatments.

Table 20: Data groups for experimental plan

Test	Treatment	Data recorded	
1	A	Side A	V_{12}, V_{13}, V_{23}
		Side B	V_{45}, V_{46}, V_{56}
	B	Side C	V_{78}, V_{79}, V_{89}
		Side D	V_{1011}, V_{1012}, V_{1112}
2	C	Side A	V_{12}, V_{13}, V_{23}
		Side B	V_{45}, V_{46}, V_{56}
	D	Side C	V_{78}, V_{79}, V_{89}
		Side D	V_{1011}, V_{1012}, V_{1112}
3	E	Side A	V_{12}, V_{13}, V_{23}
		Side B	V_{45}, V_{46}, V_{56}
	F	Side C	V_{78}, V_{79}, V_{89}
		Side D	V_{1011}, V_{1012}, V_{1112}
4	G	Side A	V_{12}, V_{13}, V_{23}
		Side B	V_{45}, V_{46}, V_{56}
	H	Side C	V_{78}, V_{79}, V_{89}
		Side D	V_{1011}, V_{1012}, V_{1112}

To complete the experimental plan the procedure shown Figure 64 in was completed for all tests.

The initial baseline EPN for all electrode couples is recorded in step 1 (Figure 58). EPN is recorded for approximately 5 minutes to determine the potential of each couple in non-corrosion conditions (baseline). In step 2 the electrolyte was introduced to each experimental unit (Insulated and Non-insulated) with care taken to avoid wetting the electrical connection of the electrodes. The electrolyte remains at the pipe surface for 20 minutes (step 3). After the wet period the electrolyte is drained from the system and discarded in step 4. The non-insulated set-up allows for visual conformation that the electrolyte is drained form the experimental unit. Because of the nature of insulation this confirmation is not possible in the insulated set-up. For this reason air is briefly injected under the insulation to ensure maximum draining.

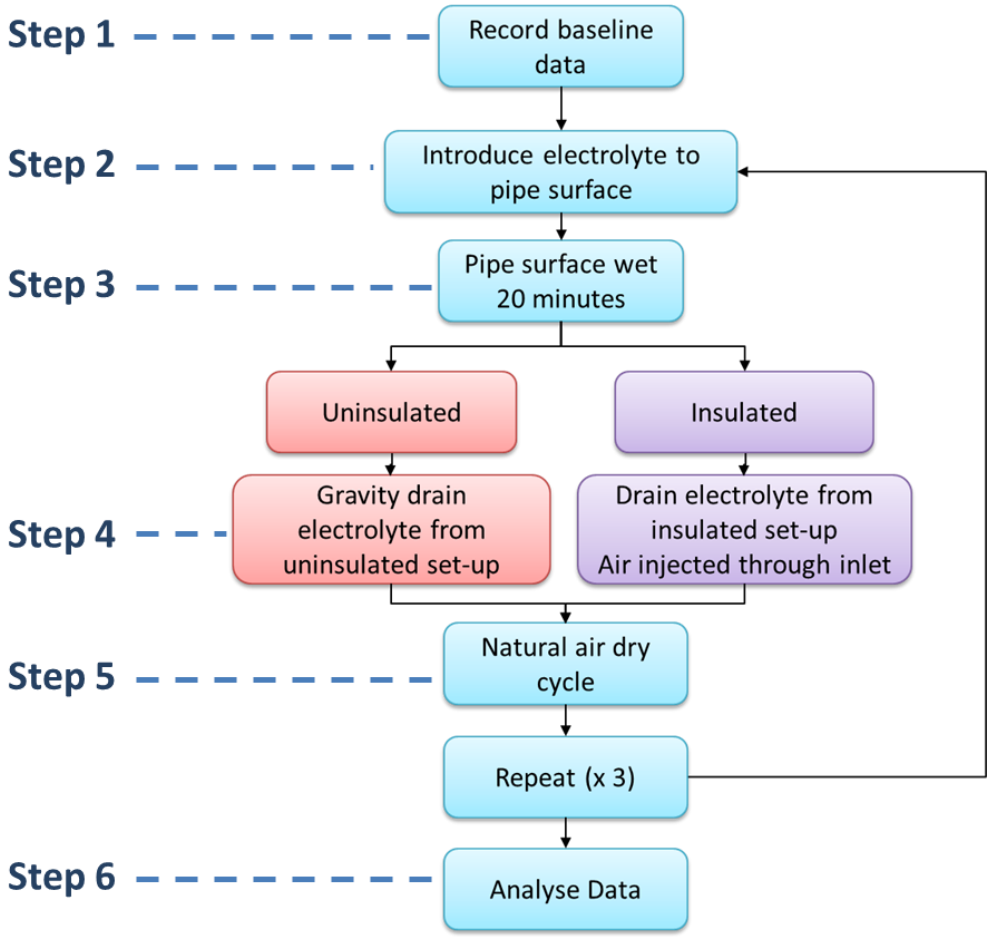


Figure 64: Experimental procedure for determination of effect of insulation on surface corrosion of pipe systems

5.4 Results and Analysis

To identify the differences in corrosion behavior of pipe systems with and without insulation three comparison methods were used. A visual inspection of the pipe electrodes was conducted to determine if differences in corrosion activity could be observed, a mass loss comparison was conducted to quantify corrosion differences and an electrochemical noise study conducted using the simplified EPN methodology developed by the Caines et al. (2016).

5.4.1 Visual Observation Comparison

Visual inspection of the electrodes was done throughout each test run. Non-Insulated electrodes were observed during the test cycle. It was not possible to observe the surface of insulated electrodes during testing due to the insulation. Table 21 lists the visual observational data.

Table 21: Visual observational data for electrode surface comparison.

Test	Treatment	Visual observation during test	Visual observation after test
Test 1	Insulated	Leak in side B insulation.	Insulation interior surface moist to touch. Electrode surface covered with corrosion product.
	Non-Insulated	Leak in side D trough. Surface appears dry quickly after electrolyte drained. No observable corrosion product in electrolyte.	Minimal corrosion product observed. Surface appears dry.
Test 2	Insulated	Minor leaks on both sides. Discolored electrolyte when drained.	Side B retained more moisture (drops seen on removal of insulation) Side A wet to touch but no drops. Side A not as tight fit to pipe surface.
	Non-Insulated	Visible corrosion on electrolyte surface. No discoloration of electrolyte observed.	Increased corrosion product with each cycle.
Test 3	Insulated	Minor leaks on both sides. Discolored electrolyte when drained.	Insulation surface wet on removal. Surface corrosion appears complete on exposed surfaces.
	Non-Insulated	Surface appears dry after electrolyte drained.	Minimal corrosion product on surface.
Test 4	Insulated	No leaks observed. Drained electrolyte appears discolored.	Surface wet after insulation removal. Surface corrosion on approximately 95% of exposed surface.
	Non-Insulated	Visible corrosion on electrolyte surface. No discoloration of electrolyte observed. Likely penetration of electrolyte to electrical connection during wet cycle 3 and 4 (Electrodes 7-9).	Corrosion product observed on approximately 90% of exposed surface. Less product observed at bottom of pipe surface.

Visual observation data indicates that there is increased corrosion product on the surface of insulated electrodes over non-insulated electrodes. Figure 65 shows the visible difference in electrode surfaces after testing.

Figure 65: Electrode surface after testing A. Insulated electrodes after Test 1. B. Non-Insulated electrodes after Test 1. C. Insulated electrodes after Test 2. D. Non-Insulated electrodes after Test 2.

Figure 65A and Figure 65B show the electrode surfaces after Test 1 (distilled water electrolyte, 1 hour drying time). Figure 65A shows the surface of insulated electrodes after completion of test 1 and Figure 65B is the surface of the non-insulated electrodes after test 1. The insulated electrodes show significantly more

surface corrosion than the non-insulated electrodes. Figure 65C and Figure 65D show the surfaces of electrodes after Test 2 (Seawater electrolyte, 1 hour drying time). The insulated electrode (Figure 65C) shows increased surface corrosion over the non-insulated electrode (Figure 65D).

5.4.2 Mass Loss Comparison

Mass loss measurements were completed for all electrodes following NACE recommended practise 0775 (NACE, 2005). All electrodes were weighed before testing and re-weighed after cleaning. Electrodes were cleaned using a 15% hydrochloric acid solution inhibited with 10g/L Dibutylthourea following NACE RP0775 (2005).

An increase in mass loss was recorded for electrodes under insulation over electrodes without insulation for all tests.

Corrosion rates (CR) were developed following NACE recommended practise 0775 (NACE, 2005) using the measured mass loss data in equation 23.

$$CR = \frac{3.65 \times 10^5 W}{A \cdot T \cdot D} \quad (23)$$

where: CR= average corrosion rate in mm/y, W= mass loss in g, A = Exposed surface area of electrode in mm^2, T = exposure time in days, and D = density of electrode metal in g/cm^2.

The statistical significance of the mass loss difference between insulated and non-insulated electrodes was determined using the unequal variance t-test (Ellison,

2009; Ruxton, 2006) with a significance level (α) level of 0.05 and can be seen in Table 22.

Table 22: Average mass loss, corrosion rate and statistical significance findings for α = 0.05

Test	Treatment	Average Mass Loss (g/m^2)	Average CR (mm/y)	Significance	
Test 1 **Distilled Water, 1 hour drying time cycle**	Insulated	5.67	192.03	Difference in Mean (g/m^2)	3.67
	Non-Insulated	2.01	67.95	Statistically Significant	Yes t=4.62, df=9, p>0.05)
Test 2 Sea Water, 1 hour drying time cycle	Insulated	16.68	450.49	Difference in Mean (g/m^2)	8.76
	Non-Insulated	7.92	213.89	Statistically Significant	Yes t=6.62, df=8, p>0.05)
Test 3 **Distilled Water, 8 hour drying time cycle**	Insulated	5.90	24.27	Difference in Mean (g/m^2)	3.89
	Non-Insulated	2.01	8.26	Statistically Significant	Yes t=2.47, df=5, p>0.05)
Test 4 **Sea Water, 8 hour drying time cycle**	Insulated	11.88	44.90	Difference in Mean (g/m^2)	2.96
	Non-Insulated	8.92	33.72	Statistically Significant	Yes t=6.10, df=7, p>0.05)

t= t-s, df = degrees of freedom, p = probability

For all tests both the average mass loss per area and the average corrosion rate was increased for electrodes under insulation over non-insulated electrodes. The difference in corrosion rate is statistically significant for all tests at a 95% level.

5.4.3 Electrochemical Comparison

To quantify the difference in corrosion behavior between insulated and non-insulated pipe a simplified EPN method was used that allows for examination of individual electrodes rather than traditional electrode pairs. For each test, four separate electrochemical cells were used, two for each set-up. Sides A and B were insulated and sides C and D were not insulated (Figure 63).

Time data for all coupled electrode pairs was analysed using the simplified EPN method (Caines et al, 2016) to isolate individual EPN for each electrode using the equations from the Caines et al (2016) methodology (Equations 1-3). To quantify non-corrosion conditions for the electrodes, a baseline potential was established for each electrode from potential measurements during the time before any electrolyte was introduced to the electrodes. This baseline potential is needed to quantify the measurement noise due to the open circuit condition when no electrolyte is present. Without the presence of electrolyte as seen in Figure 66A, there is no complete circuit and the potential measurement between two points should be zero V. A closed circuit as seen in Figure 66B is only possible when an electrolyte is present.

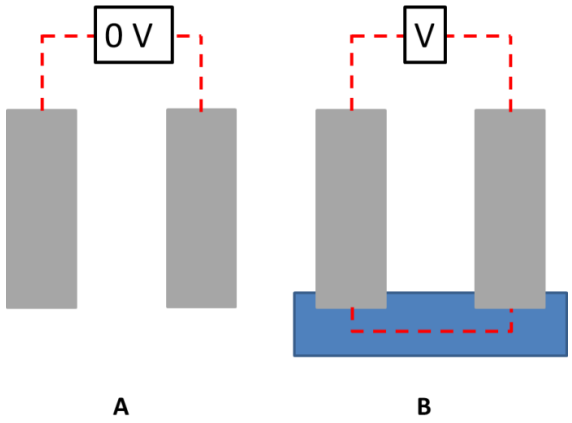


Figure 66: Theoretical explanation of baseline EPN

If the measured EPN is below the baseline reading, the circuit is considered incomplete and no corrosion is occurring. If the EPN reading is above the baseline, corrosion conditions are present and corrosion is indicated. Baseline measurements for all tests are listed in Table 23 .

Table 23: Baseline EPN for initial dry, non-corrosion condition

Test	Treatment	Baseline Potential (average μV)
Test 1	Insulated	0.25
	Non-Insulated	0.18
Test 2	Insulated	0.14
	Non-Insulated	0.14
Test 3	Insulated	0.23
	Non-Insulated	0.28
Test 4	Insulated	0.24
	Non-Insulated	0.87

Measured EPN less than the baseline is considered non-active where no corrosion is indicated. Based on Table 23 values the baseline value is set to 1μV. Any

measurement above 1 μV is considered active and corrosion is indicated during these periods. All electrode data was analysed to determine the amount of time during each test that active corrosion was indicated. Table 24 lists the portion of the total test time that the electrode EPN measurements indicated active and non-active conditions. Column 3 (Wet) of Table 24 indicates the portion of total test time where the electrolyte was introduced and held at the pipe surface before draining. For all tests the total wet period for the complete experiment was one 1 hour. This is approximately 20 % of the total test time of tests 1 and 2 (1 hour drying time) and less than 5% of tests 3 and 4(8 hour drying time).

Table 24: Proportional average time of wet and dry periods

		Wet % of Total test time	Dry % of Total test time	Active % of Total test time	Non-active % of Total test time
Test 1	Insulated	20	80	97	3
	Non-Insulated	18	82	20	80
Test 2	Insulated	23	77	67	33
	Non-Insulated	27	73	26	74
Test 3	Insulated	4	96	98	2
	Non-Insulated	4	96	4	96
Test 4	Insulated	3	97	69	31
	Non-Insulated	3	97	13	87

The active and non-active times indicated in columns 5 and 6 in Table 24. These values indicate the portion of time where the measured EPN is above the 1 μV baseline.

For non-insulated electrodes the active portion of the test is similar to the amount of time of electrode wetting. This indicates that when the electrolyte is drained, corrosion does not continue for non-insulated electrodes.

For insulated electrodes, all tests indicated an increase in active time over the time the electrodes are wetted. Electrolyte was introduced under insulation for less than 25% of the total test time for tests 1 and 2 however the amount of time indicating active corrosion is significantly higher; 97% and 67% respectively. For tests 3 and 4 the electrolyte was introduced for less than 5% of the total test and the amount of time of active corrosion is significantly higher at 98% and 69% respectively. This indicates that there is more opportunity for corrosion to occur under insulation than in non-insulated pipes.

A sample of the isolated electrode data for insulated electrodes and non - insulated electrodes from Test 1 is shown in Figure 67. Periods of Wet and Dry are identified and differences in behavior can be observed. Wet periods are the times when the electrolyte is introduced and held at the pipe surface. Dry periods are when the electrolyte is drained from the pipe surface until the introduction of the next wet cycle.

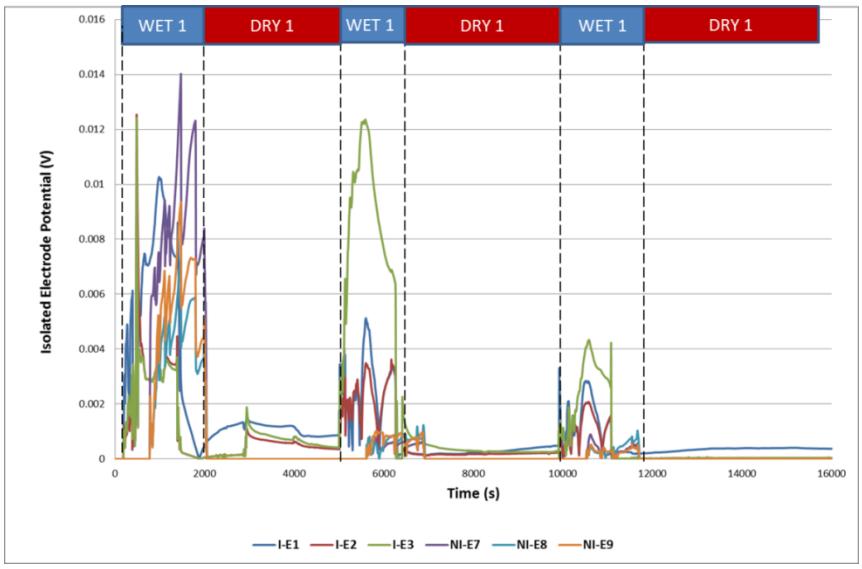


Figure 67: Test 1 (distilled water, 1 hour cycle) Isolated electrode potential

Figure 67 demonstrates the three cycles included for each test. Similar behaviour can be seen for all electrodes during the wet periods of the test. Differences in behaviour between insulated and non-insulated electrodes can be seen during dry periods. To further highlight these differences the first wet and dry periods of Test 1 are shown in Figure 68.

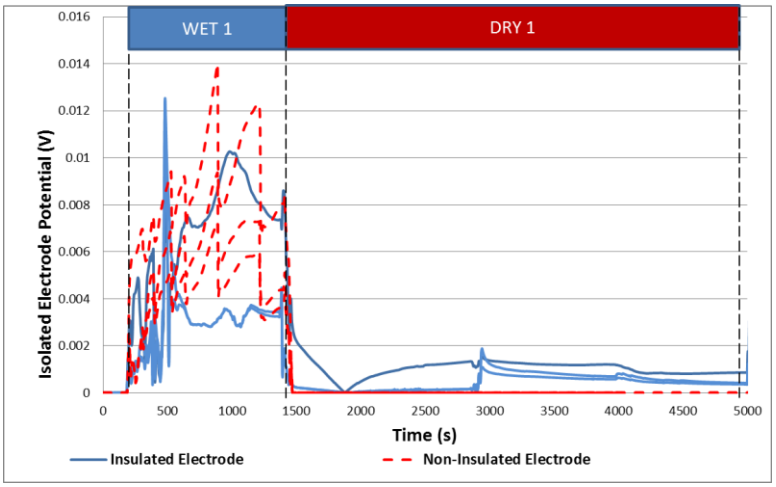


Figure 68: Wet period 1 and dry period 1 for Test 1 Isolated electrode potential.

To highlight the difference in behaviour between insulated and non-insulated electrodes all insulated electrodes are shown as solid lines and all non-insulated electrodes are shown as dashed lines in Figure 68. Similar behaviour can be seen during the wet period and the differences in behaviour during the dry period become more obvious.

Closer examination of dry period 1 is shown in Figure 69.

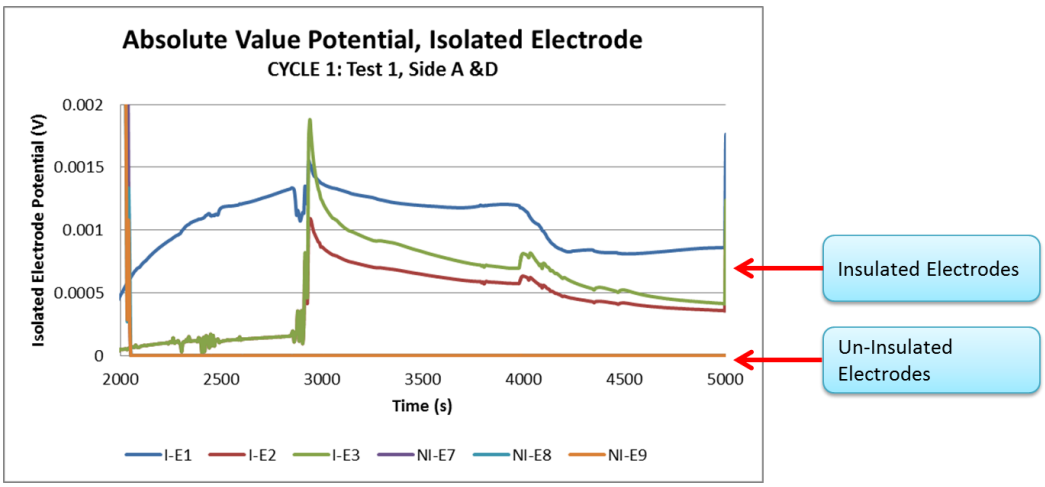


Figure 69: Test 1 Isolated electrode potential, CYCLE 1- Dry

Figure 69 shows a significant difference in the electrochemical behaviour of the insulated electrodes and non-insulated electrodes. The insulated electrodes show continued electrochemical activity during the dry period and the non-insulated electrodes do not demonstrate any electrochemical activity during dry period 1.

To begin to quantify this observed increase in corrosion activity, the EPN of each electrode was examined. An increase in EPN above the baseline level is considered an active period where conditions are favorable for corrosion.

The EPN data was segregated into wet and dry periods for each electrode. The mean of EPN for each period was calculated. The mean EPN for all periods is shown in Table 25 to illustrate the effect of insulation on corrosion behaviour of pipes. The dry period mean EPN for the non-insulated electrodes indicate a return to non-corrosion conditions when these averages are examined in comparison to the baseline potential.

Table 25: Mean EPN by cycle period

Test	Treatment	Baseline Mean EPN (μV)	Wet 1 Mean EPN (μV)	Dry 1 Mean EPN (μV)	Wet 2 Mean EPN (μV)	Dry 2 Mean EPN (μV)	Wet 3 Mean EPN (μV)	Dry 3 Mean EPN (μV)
Test 1 distilled, 1 h dry time	Insulated	0.2	3220.7	320.3	3304.8	139.4	2506.4	36.2
	Non-Insulated	0.2	3355.6	0.6	548.2	0.3	429.7	0.2
Test 2 Sea, 1 h dry time	Insulated	0.1	16323.1	2489.4	19111.7	1675.4	13986.9	20.4
	Non-Insulated	0.1	4874.3	0.2	3984.9	0.2	1716.2	0.3
Test 3 distilled, 8 h dry time	Insulated	0.2	9265.8	1033.6	4676.0	1345.8	4896.5	581.2
	Non-Insulated	0.3	8823.3	1.0	6145.0	0.3	2010.6	0.2
Test 4 Sea, 8 h dry time	Insulated	0.2	15562.2	1125.9	10191.2	2335.8	5418.6	1241.8
	Non-Insulated	0.9	4996.8	0.5	6517.2	0.2	7719.8	370.0

All average dry potential are less than 1 μV except for dry periods 2 and 3 for Test 4. One side of the experimental set-up for Test 4 was observed to allow the electrolyte to come in contact with the electrical connection of each electrode. This contact may cause corrosion between the connection wire and the electrode and result in elevated EPN readings that do not correspond to bulk electrode corrosion.

If these readings are excluded from analysis, the mean dry period EPN reduces to 0.2 μV and 1.2 μV respectively.

The mean dry period EPN for the insulated electrodes show a reduction from the wet period mean EPN however it does not return to non-corrosion potential of the baseline (<1 μV). This indicates that wetness continues under insulation allowing for the continued circuit connections for corrosion to continue.

The statistical significance of the average potential difference between insulated and non-insulated electrodes was determined using the unequal variance t-test (Ellison, 2009; Ruxton, 2006) after outlier removal using the Peirce method (Ross, 2003) with a significance level (α) level of 0.05.

A single tail analysis was used to test the null hypothesis (Ho) that Corrosion activity is not increased by the application of insulation to pipe systems after an electrolyte is introduced to the pipe surface versus the research hypothesis (HR) that corrosion activity is increased by the application of insulation to pipe systems after an electrolyte is introduced to the pipe surface.

H_o: $\mu_I=\mu_N$ H_R: $\mu_I>\mu_N$

Table 26 lists the findings of this analysis. This analysis found that the increase in the EPN mean for insulated electrodes over non insulated electrodes are all statistically significant at 95% confidence except for two of the dry period (Dry cycle 1 for Test 1 and Dry cycle 2 for Test 4). When the significance level is lowered to 94%, the difference becomes statistically significant in all periods. This analysis

allows for the acceptance of the research hypothesis that corrosion activity is increased when insulation is applied to pipes.

Table 26: Statistical significance of EPN mean for insulates versus non insulated electrodes, α = 0.05

Test	Significance	Dry 1	Dry 2	Dry 3
Test 1	Difference in Mean (mV)	0.320	0.139	0.036
	Statistically Significant	No t=1.88, df=5, p>0.05)	Yes t=2.38, df=5, p>0.05)	Yes t=10.84, df=4, p>0.05)
Test 2	Difference in Mean (mV)	2.48913	1.67525	0.02006
	Statistically Significant	Yes t=2.20, df=5, p>0.05)	Yes t=2.20, df=5, p>0.05)	Yes t=2.46, df=5, p>0.05)
Test 3	Difference in Mean (mV)	1.033	1.345	0.581
	Statistically Significant	Yes t=11.384.22, df=4, p>0.05)	Yes t=4.39, df=5, p>0.05)	Yes t=2.26, df=5, p>0.05)
Test 4	Difference in Mean (mV)	1.125	2.329	0.871
	Statistically Significant	Yes t=2.03, df=5, p>0.05)	No t=2.01, df=5, p>0.05)	Yes t=5.00, df=5, p>0.05)

5.5 Discussion

The results of this study clearly indicate that there is increased corrosion on surfaces of insulated pipes than uninsulated pipes. All three comparison methods,

observational, mass loss, and EPN, indicate an increase in corrosion for pipes under insulation.

5.5.1 Visual Observation

For all tests a visual difference was observed in the surface condition of the electrodes after testing. An increase in visible surface corrosion was seen when insulation was removed over the amount of visible corrosion to the non-insulated surfaces. This difference was most clear in Tests 1 and 3, the distilled water tests as the non-insulated electrodes showed very little visible surface corrosion. The surface of all electrodes exposed to seawater (insulated and non-insulated) showed significant corrosion product however increased corrosion product on insulated electrodes was still apparent. Based on visual observation, there is increased corrosion for electrodes under insulation than electrodes without insulation. This increase in corrosion product visible on the surface of insulated samples is likely due to the moisture retained by the insulation. When removing the insulation, moisture was observed on the inside surface of the insulation and the sample surface appeared damp. This prolonged exposure to an electrolyte increases the opportunity for corrosion and increases the severity of corrosion.

5.5.1.1 Observed Experimental issues

Issues with experiments are possible and can affect the outcome. The most significant issue observed was occasional leaking near the electrode connection (Figure 70). This was observed in Test 3 and Test 4.

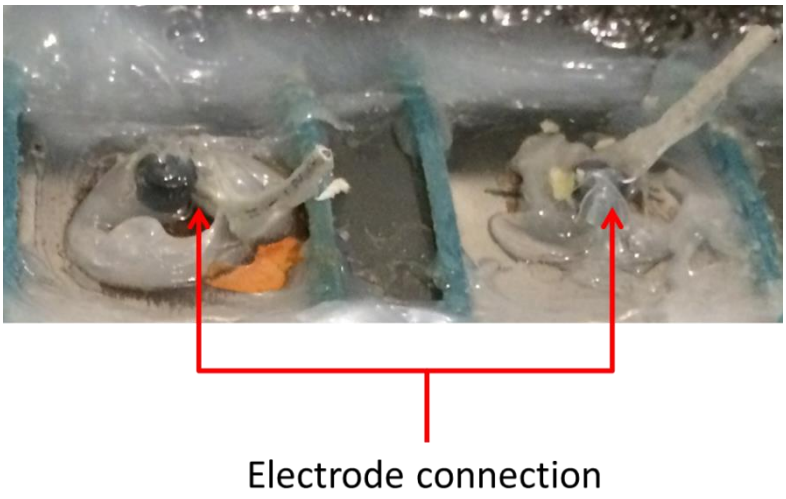


Figure 70: Electrode electrical connection

Leaking near the electrode connection can cause recording of EPN for corrosion between the wire connection and the electrode rather than the corrosion occurring in the bulk of the electrode. This was observed during the dry periods for test 4 on some non-insulated electrodes. This caused higher than expected EPN measurements that indicted continued corrosion of non-insulated electrodes after the electrolyte was removed from the surface.

5.5.2 Mass Loss

Mass loss measurements indicate a clear increase in mass loss and average corrosion rate in electrodes under insulation. For each test, increased mass loss and corrosion rate was found for insulated electrodes over non-insulated electrodes. These increases were found to be statistically significant at 95%. The cause of this increase is attributed to the moisture retained by the insulation

allowing increased corrosion time and therefore increased overall mass loss in insulated samples over non-insulated samples.

Previous work by the Caines et al. (2016) indicates that there is a relationship between EPN and corrosion rate. In this work the authors found that there was a correlation between EPN area (V·s) and the corrosion rate developed from mass loss data.

For this study, the average corrosion rate from the mass loss studies somewhat correlates with the EPN area. Figure 71 shows the trend for increased corrosion rate with increased EPN area measurements. For the 1 hour tests (Tests 1 and 2) this relationship is somewhat strong at an R^2 value of 0.78 however the 8 hour drying time tests (Tests 3 and 4) show limited correlation (R^2 = 0.40) between EPN area and CR.

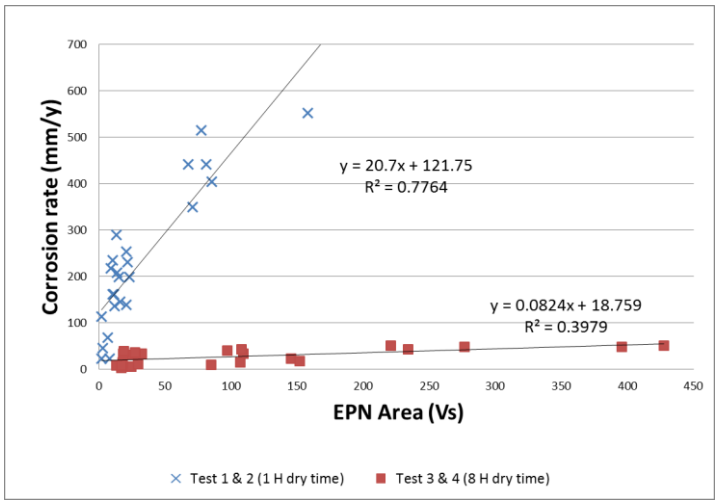


Figure 71: Relationship between EPN and corrosion rate for all tests

Examination of the 8 hour drying tests individually shown in Figure 72 indicate that each test individually demonstrates a correlated relationship but do not demonstrate a relationship when viewed together.

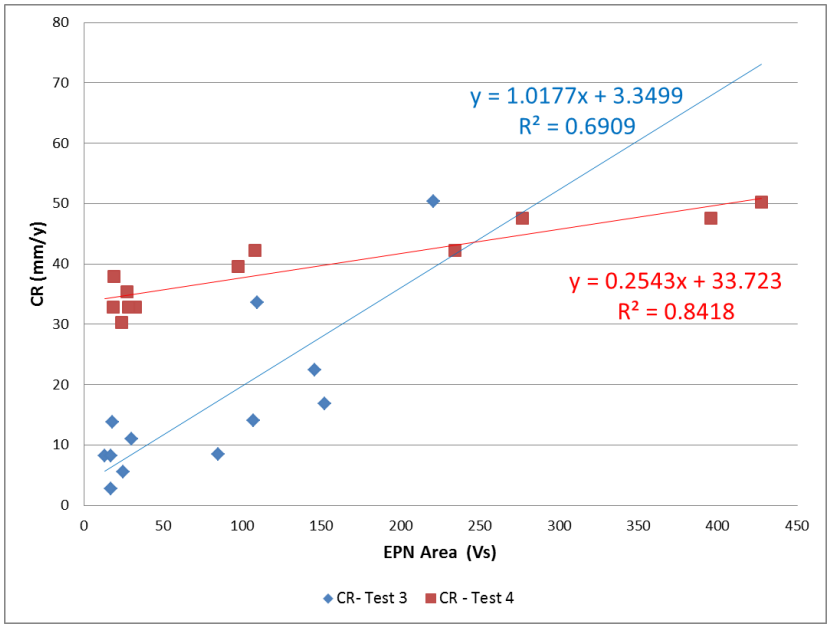


Figure 72: Relationship between EPN and corrosion rate for 8 hour dry time cycle tests 3 and 4.

Mass loss measurements initially introduced in the work by the authors (Caines et al 2016), longer term testing is needed to fully capture the relationship between recorded EPN and corrosion rate. These results also indicate that the cyclic nature of CUI may require additional study to determine the effect on recorded EPN over the long term.

5.5.3 Electrochemical Comparison

The simplified EPN measurements showed similar magnitude of readings for all electrodes during the wet period. This indicates that corrosion is comparable for

both insulated and non-insulated pipes when under direct contact with an electrolyte and differences in total corrosion of electrodes can be attributed to the differences in the dry periods. This study also demonstrates the significant corrosion activity during dry periods for insulated electrodes. During the dry period significant differences in electrochemical potential was found. Increased EPN was found for insulated electrodes indicating higher corrosion activity under insulation when the electrolyte is removed. The non-insulated electrodes showed very little electrochemical activity during the dry period while the insulated electrodes demonstrated ongoing electrochemical activity. This continued activity is therefore the consequence of insulation.

Insulation increases drying time of the pipe surface allowing additional corrosion. After each test, the surface of the insulation was found to retain some electrolyte.

Non-insulated pipes are exposed to natural airflow to aid in the speed of drying as there is no mechanism present to retain electrolyte at the pipe surface. Observation of the non-insulated electrode surfaces showed quick drying after the electrolyte was drained. Cyclic observation of the insulated electrode surface was not possible however after testing moisture was observed on the internal surface of the insulation when removed from the pipe. Figure 73 illustrates this retained electrolyte. The insulation is essentially a closed system that retains moisture at the pipe surface even when the electrolyte is drained.

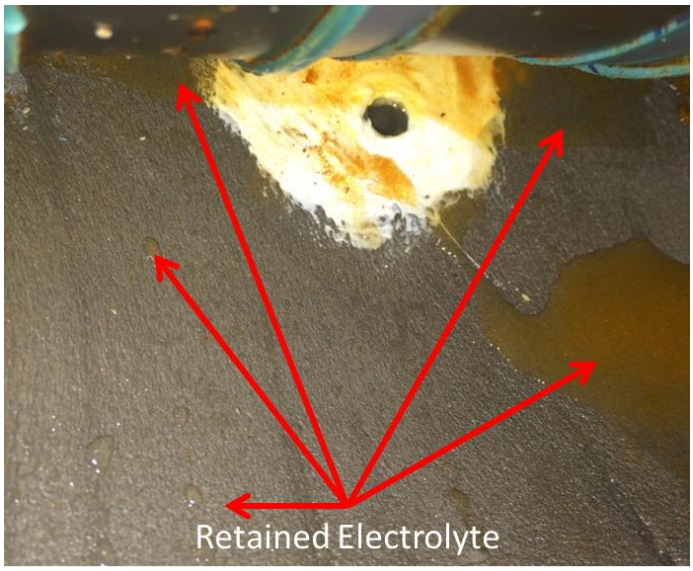


Figure 73: Typical retained moisture under insulation after testing.

The additional time needed for the insulated pipe electrode surface to dry can be determined from the experimental set-up. As the surface dries, the electrode EPN will return to the baseline potential (<1 μV) indicating there is no longer an electrolyte available to create corrosion conditions and complete the circuit. To demonstrate this application, an additional test using distilled water and natural sea water was completed on insulated electrodes and data recorded for one wet and dry cycle with measurements taken until readings returned to the <1 μV range indicating an open circuit and therefore dry surface. The complete cycle is shown in Figure 74. The drying time for distilled water was approximately 12.9 days and the drying time for natural salt water was approximately 14.7 days.

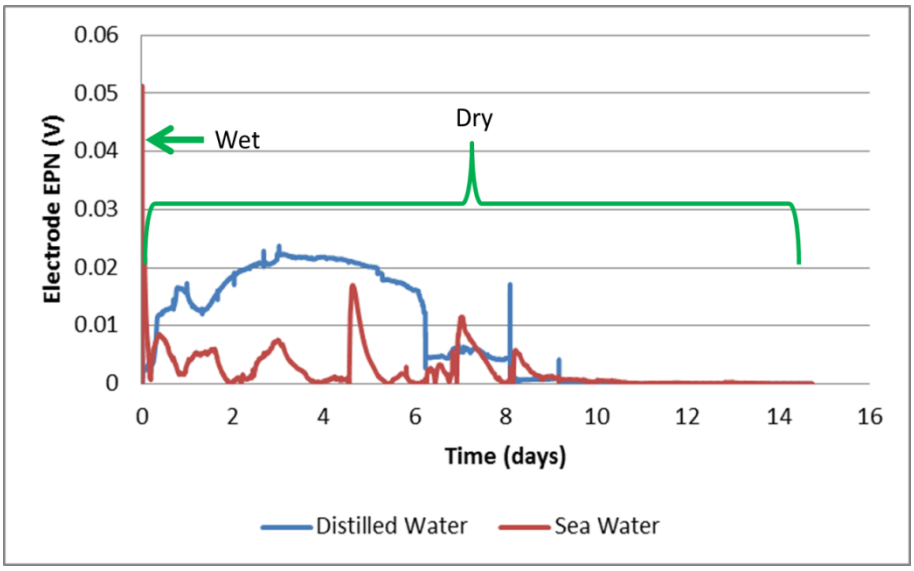


Figure 74: Wet and dry cycle to determine drying time for electrodes under insulation with distilled water and natural sea water.

Closer examination of days 12-15 of the test is shown in Figure 75. This illustrates the reduction in EPN to below 1 μV for both distilled and seawater electrolytes and highlights the EPN readings that indicate the surface is dry.

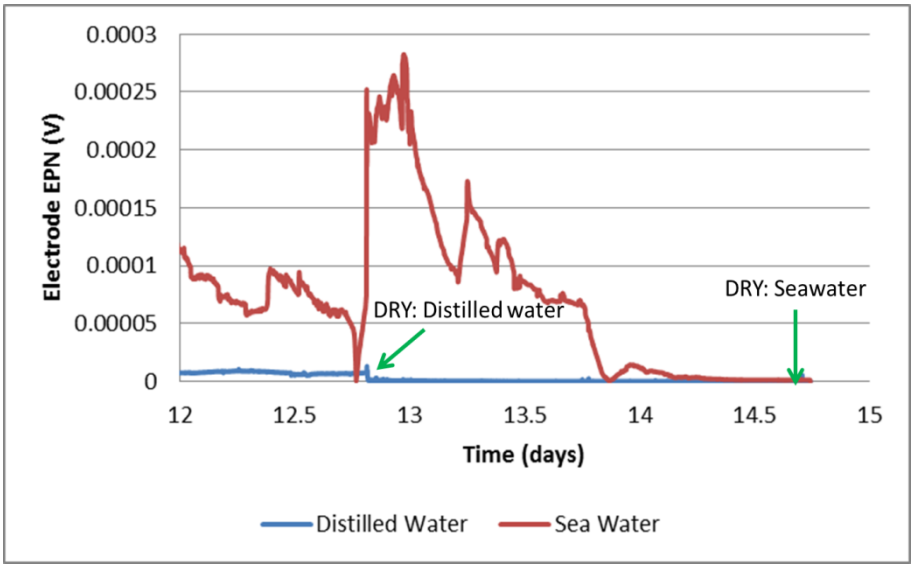


Figure 75: Dry times for distilled and seawater

Drying times for Non-Insulated electrodes were found from the original study measurements as all test data indicates drying time within the first minute after electrolyte was drained. No additional testing was required.

Drying times are specific to the situation; insulation type, amount of electrolyte introduced and the operational conditions of the system. For example smaller amounts of electrolyte penetration to the pipe surface at elevated operational temperatures would likely have a reduced drying time however this time is expected to remain longer than the time for a non-insulated pipe under the same conditions.

5.6 Conclusions

This work supports the long held belief that corrosion of insulated components is more severe than corrosion on uninsulated pipe systems under similar conditions. Significantly more corrosion was found for electrodes under insulation than electrodes without insulation. This difference was confirmed with visual inspections, mass loss data, and electrochemical noise measurements.

Visual inspection of the electrode surfaces showed more visible corrosion on insulated electrodes than non-insulated electrodes.

Increased mass loss and corrosion rates were found for insulated electrodes over non-insulated electrodes. These increases were statistically significant at a 95% level.

Analysis of EPN data shows that active conditions for corrosion continue during the dry period for insulated electrodes and not for non-insulated electrodes. The percentage of total test time with active corrosion conditions was increased from 20% to 98% for non-insulated electrodes and to 67% for insulated electrodes with a 1 hour drying cycle. The percentage for the 8 hour drying cycle was increased from less than 13% for non-insulated electrodes to over 69% for insulated samples.

The difference in EPN mean for insulated and non-insulated electrodes was found to be statistically significant (at 94%) resulting in the acceptance of the research hypothesis that insulation increases corrosion on pipe surfaces.

For tests with a one hour drying cycle a relationship between the EPN area and the corrosion rate was found with an R^2 value of 0.78.

For tests with an 8-hour drying cycle no relationship ($R^2 = 0.40$) was found between the EPN area and the corrosion rate.

When analysed separately, the 8-hour drying cycle tests demonstrated a correlated relationship. The distilled water test had a correlation of $R^2 = 0.69$ and the seawater test had a correlation of $R^2 = 0.84$.

The increase in corrosion activity under insulation is due to retained moisture at the pipe surface by the insulation. The closed system of insulation reduces evaporation and allows for continued corrosion. Insulation increases drying time of the pipe surface allowing additional corrosion:

- Drying times for non-insulated electrodes were all recorded as less than 1 minute.
- Drying time for insulated electrodes with one 20-minute wet cycle with distilled water was 12.9 days.
- Drying time for insulated electrodes with one 20-minute wet cycle with sea water was 14.7 days.
- Drying times are specific to a situation; insulation type, amount of electrolyte introduced and the operational conditions of the system will all impact the drying time for surfaces under insulation.

If moisture penetrates pipe insulation and can reach the pipe surface this work shows there is a prolonged opportunity for corrosion activity due to retained moisture under the insulation. The reasons for moisture penetration to the pipe surface of insulated components are beyond the scope of this work, however, methods and design options to limit the introduction of moisture to the pipe surface of insulated pipes must be developed and predictive methods for the likelihood of corrosion conditions occurring must be discovered.

In addition, these results indicate that the removal of insulation would decrease the opportunity for corrosion and increase safe, continuous operations. The increase in corrosion for insulated pipes demonstrated in this research indicate that care should be taken when adding insulation to components to ensure insulation is only used where required.

The simplified method (Caines et al, 2016) was successfully applied to study CUI. This success justifies the need for expanded application of this simplified method to:

- Laboratory testing to further the understanding of the relationship of EPN to corrosion rate.
- Field testing to generate real time data of surface corrosion under insulation.
- Develop corrosion rate prediction models for asset corrosion under insulation.

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6.0 Conclusions and Recommendations

6.1 Conclusions

The aim of this research was to further the understanding of asset corrosion under insulation. The study was planned with two distinct objectives to fill knowledge gaps. The following sections will summarise the findings of this research as they contribute to the achievement of these objectives.

6.1.1 Corrosion Under Insulation Data Generation

Through the systematic analysis of six categories of pitting corrosion the state of understanding for each was determined. Depth of knowledge of pitting corrosion rate modeling and pitting mechanism were found to be significantly lower than other pitting categories. These findings indicated the need for long term data. To generate the required information a comprehensive experimental plan was developed. This plan develops a field test procedure to study corrosion under insulation (CUI) in marine environments that ensures that data collected is representative of CUI developed in the offshore industry. Also included in the plan is the development of a laboratory test to realistically predict long term asset corrosion. The experimental design was completed and the facilities and equipment installed. The monitoring and analysis of the ongoing experiment will be completed over the next three years by the C-RISE research group. Beyond the field, characterization, and accelerated testing developed in Chapter 3 for this work, additional laboratory tests were developed and completed to contribute to

data generation for the study of CUI. These tests yielded a controlled comparable data for future analysis and aided in the development of a simplified method for data generation.

6.1.2 Continuous Monitoring technique development

In addition to the development of field and laboratory testing for characterization and acceleration, the completed study and analysis of pitting corrosion indicated a need for a new technique to determine corrosion rates and mechanism from on-line monitoring. This research developed, verified and applied a simplified EPN method to monitor corrosion. This method can be used to recognise different corrosion mechanisms (localized/uniform) and to estimate corrosion rates.

This simplified method uses isolated electrode EPN records to predict corrosion rate of each individual component. A relationship between isolated electrode EPN, mass loss and corrosion rate was established. This confirms EPN as a promising way to monitor corrosion.

This research also validated the relationship between isolated EPN and corrosion rate and that this simplified method can distinguish between different types of corrosion.

The simplified method aided in determining that there is increased corrosion activity under insulation due to retained moisture at the pipe surface. If moisture penetrates the insulation and can reach the surface this work shows the opportunity for corrosion activity due to retained moisture under the insulation can

be captured and analysed using the simplified EPN method. The Caines et al (2016) simplified method was successfully applied to study CUI. This success in laboratory testing allows for the expansion of the technique to intensified laboratory and field applications to further validate the methodology and develop predictive models. This is a significant step to create a continuous monitoring technique to help reduce the impact of corrosion on assets under insulation.

6.2 Recommendations

6.2.1 Corrosion Under Insulation Data Generation

Further research is needed to continue to the work of this thesis. Understanding the effects of corrosion on assets under insulation is important to controlling and preventing this issue. A corrosion rate model for CUI in offshore environments must be developed. This can only be developed when the variables that affect this type of corrosion are understood and the interactions between variables determined. The CUI information gathered through the field testing designed in this thesis will characterise the phenomenon and open new strategies for prevention. Once this is completed, additional information should be created to further develop the model to increase accuracy and reliability. This additional information includes:

- How and why moisture penetrates insulation: This information is needed to improve design and to fully develop risk assessments on the installation of insulation on assets.

- The effect of retained moisture under insulation in terms of composition: When an asset is subjected to cyclic wetting there is an opportunity for ion build-up on the surface which may impact the concentration of subsequent moisture allowed to reach the surface.
- The effect of temperature fluctuations on corrosion behaviour under insulation: Process temperatures in offshore operations are varied and temperature has a known effect on corrosion.
- The effect of microbiological influenced corrosion under insulation: With retained moisture at the surface of insulated assets the effect of trapped microbials must be assessed.

6.2.2 Continuous Monitoring Technique Development

To develop a continuous monitoring technique for asset under insulation in offshore operations, the simplified EPN methodology developed in this thesis should be expanded and development continued.

To fully develop this simplified method for expanded application, additional testing is required to characterize the relationship between isolated electrodes and their EPN. Future work includes:

- Longer term testing: Required to characterise the EPN / CR relationship
- Dissimilar electrodes test: Required to validate the application of the method for non-identical electrodes.
- Develop relation model between EPN and corrosion rate

The simplified method will be applied to the field test plan and this additional information will further validate the use of this methodology to in-situ operations. To develop this methodology for offshore operations, research is needed in how to directly apply this technology to assets in-situ. The equipment changes to adapt to an operational setting must be evaluated and the inclusion or adaption of a three electrode system must be developed.

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